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AD 603 437

SPACE SCIENCES LABORATORY

AEROPHYSICS SECTION

THE CHEMICAL KINETICS OF SODIUM IN RE-ENTRY

By

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135 p

Re - 400

mf - 1.00

Part of the work described in this report was carried out under Contract AF 04(694)-486. The report was originally issued in the ARP series as 64SD810.

R64SD33
April 1964

MISSILE AND SPACE DIVISION

GENERAL  ELECTRIC

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ABSTRACT

Sodium is important to reentry because of its contributions to radiation and electron density. It is shown here that neither its radiation nor its electron density can be expected to be in equilibrium. A study of the complete chemical kinetics of sodium is described herein. The radiation is subject to considerable "collision limiting" (non-equilibrium excitation and deexcitation). The ionization processes cannot be assumed to be instantaneous and the deionization processes are very slow. The major reaction is the ionization-deionization system, found to be $\text{Na} + \text{O} \rightleftharpoons \text{Na}^+ + \text{O}^-$, although other reactions, both of this type and other types, contribute appreciably, depending on the conditions. Included in this report is a recommended chemical system, with rate constants, for use in any non-equilibrium calculations of the effects of sodium in reentry.

I. THE IMPORTANCE OF SODIUM KINETICS IN REENTRY

A. Sodium as an Observable

Sodium is important under reentry conditions as an observable, both as an emitter of visible radiation and as a contributor to the electron density. Sodium is an easily ionized material. Its ionization potential is 5.14 electron volts.* Such a low ionization potential tends to cause relatively high degrees of ionization of sodium. For most conditions of interest in reentry, sodium is almost completely ionized if equilibrium exists. Thus any appreciable amount of sodium contributes greatly to electron densities. Figure 1 illustrates the extent of equilibrium sodium ionization as a function of temperature. These are for several concentrations of sodium and for conditions such that the concentrations of sodium ions and of electrons are equal.

Sodium is, of course, a well-known radiator. The resonance D-lines at 5890 and 5896 Å are very strong lines and the presence of neutral sodium at any moderate temperature produces considerable emission. The equilibrium sodium D-line radiation per neutral sodium atom is given as a function of temperature in Figure 2. It must be noted, however, that ionized sodium atoms do not directly produce this radiation. If the sodium is ionized to a considerable degree, there will be little radiation. The equilibrium sodium D-line radiation per sodium atom (neutral or ionized) is given as a function of temperature in Figure 3. One other contributing factor would be the effect of sodium compound formation. The bonding of sodium to other species would also make it unavailable as a radiator. This effect could be quite important at low temperatures.

* This compares with 15.58 for N_2 , 12.08 for O_2 , 9.25 for NO, 14.54 for N, 13.61 for O, 5.39 for Li, 3.89 for Cs, 6.11 for Ca, 12.99 for CH_4 , 14.01 for CO.

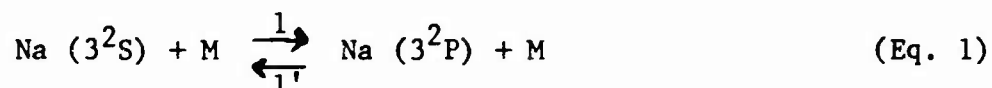
The energy levels of sodium are shown in Figure 4. The transitions giving the D-line doublet are drawn in. Of course, other transitions occur, those between S and P, between P and D, between D and F, between F and G, and between G and H levels being the permitted and hence, in general, the strongest emissions. The D-line is by far the most important because it requires the least energy to populate the upper state and because the probability of the transition is very high. The ionization continuum is also shown here, above 5.14 e.v.

B. The Effect of the Chemical Kinetics of Sodium

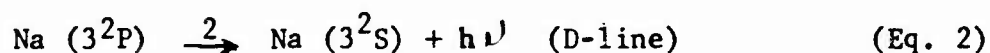
The amount of sodium ionization and of sodium D-line radiation is determined by the chemical kinetics, that is, by the chemical reactions and their rates. The complex mechanisms which account for the ionization may be slow to ionize sodium to the equilibrium degree in the time available in the boundary layer. Calculations discussed later indicate such a situation for some conditions of interest. Even more of an effect is that of sodium on deionization. Once sodium is ionized, it will deionize very slowly and the corresponding electron density will persist at higher-than-equilibrium levels for appreciable times, at least for some conditions of interest. The analysis and calculations presented later present some of the details of the kinetics involved.

The chemical kinetics of the sodium radiation is also complex. Since, as mentioned above and illustrated in Figure 3, the radiation depends on the fraction of the sodium which is ionized, the kinetics of ionization and of deionization are important to the amount of radiation. Also, as mentioned in the previous section, the sodium tied up in compounds is unavailable for D-line radiation and the kinetics of sodium compounds are important. Further, in order for the radiation from a given concentration of free neutral sodium

atoms to be its equilibrium value, the collisional excitation and deexcitation ("quenching") must have equal rates. This may be seen by the following equations



At equilibrium, the rates of this reaction in the forward and reverse directions are equal, i.e., $v_1 = v_{1'}$, and the rate of the reaction which emits the D-line radiation



must be much smaller so that

$$v_1 = v_{1'} + v_2 \simeq v_{1'}$$

If this is not so, the rate of deexcitation tends to be greater than that of excitation and the concentration of the excited state (3^2P) must become lower. This lowers the emission to a value below equilibrium. This phenomena is known as collision-limiting. Non-equilibrium radiation also occurs if some other reaction forms or consumes the excited sodium (3^2P) at a rate which is appreciable relative to those of equation 1. Such reactions may be some chemi-excitation or chemi-deexcitation reactions or the radiative deionization into some excited state of the neutral sodium atom formed.

C. The Occurrence of Sodium

Sodium is not a major constituent of the gas around a reentry vehicle but appreciable amounts of it may be present and have the forementioned effects on radiation and electron density. Such sodium may arise in two ways.

Sodium may, of course, be present in substantial amounts in nose cone material. Ablation of this material would then introduce sodium into the boundary layer and wake regions. The amounts in this region need not be large to cause large effects. It appears that less than one part per million in these regions could be important.

Some sodium is also present in the normal atmosphere. Rough measurements of this have been made. However, such measurements tell only the amount of free neutral sodium atoms. Our present knowledge of the thermodynamics and kinetics of sodium in compounds does not permit any accurate estimation of the amount of sodium present in compounds. This may, indeed, be much greater than the free sodium at any altitude, and especially so at the altitudes of greatest interest to reentry, say below 250,000 feet. A thorough consideration of and more information on this problem is needed. It is a definite possibility that appreciable amounts of sodium could be introduced into the system from the ambient atmosphere.

II. THE CHEMICAL KINETICS OF SODIUM

A. The Important Species in the System

Sodium will occur in many forms in the reentry flow field. While the free neutral atom and the atomic ion are of the most direct importance, these can not be considered here without considering numerous other forms.

The free neutral atom is present primarily in its ground state, that is, as Na (3^2S). The many other electronic energy levels available to it will also be populated to some extent. These energy levels are shown in Figure 4. Of course, the higher the energy of a level, the lower its population, in general. Each of these levels is important in the various reactions. If the distribution among the various energy levels is the equilibrium distribution, there is little need for considering the individual states. If, however, this is not the case, the rates of populating and depopulating the excited states must be considered. Thus the rates of direct excitation and deexcitation processes and of the various chemical reactions involving the excited states become important.

Of particular importance is the state Na (3^2P) the upper state of the sodium D-lines emission. If this is not in equilibrium with the ground state and other excited states, the rate of D-line radiation will not be the equilibrium value and the rates of some chemical reactions may be appreciably affected.

This ion is formed rather readily from the free neutral atom since only 5.14 e.v. are required for the ionization. The mechanisms forming and consuming the ion are discussed in the next section. In spite of the low ionization

potential, it can not be assumed that the ions and free neutral atoms are in equilibrium since the ionization processes require appreciable time. The sodium ion can be assumed to be entirely in its ground state, $\text{Na}^+ (2^1\text{S})$ since the first excited level is 32.84 e.v. above the ground state.

Diatomic sodium ions, Na_2^+ , may also occur. Under certain conditions, these may be important, particularly in deionization. However, their importance is decreased by high temperature, low density, and low sodium mole fractions. The diatomic sodium molecule, Na_2 , is also adversely affected by these factors and is even less likely to be of importance.

Sodium also forms a negative ion, Na^- , but its electron affinity is quite low and the electron is readily detached. Thus this negative ion is not important for the conditions of interest here.

Sodium will rather readily bond to oxygen atoms and molecules, hydrogen atoms, hydroxyl radicals, and many other species less likely to be of importance here. Such bonding occurs by various types of chemical reactions and forms such species as NaO , NaO_2 , NaH , and NaOH , each of which is fairly stable, although more information on some of the bond energies is badly needed.

These are the principal species of sodium of interest here. However, other species not containing sodium are of importance to the chemical kinetics of sodium. Their concentrations and, in some cases, their chemical kinetics must be known to make a study of the chemical kinetics of sodium. Among the species of the nitrogen-oxygen system which must be so considered are O , O_2 , NO , NO^+ , O^- and O_2^- . Organic materials also affect sodium, reacting with it in several ways. Such species as H , H_2 , CH , OH , H_2O , OH^- and CHO^+ require consideration.

B. Mechanisms of Ionization

Several mechanisms are important to sodium ionization. The relative importance is dependent on the conditions, the temperature and density of the system, and the concentrations of some of the species involved in the reactions. Since the different mechanisms require considerably different energies, temperature plays a major role by its effect on the rate constants of the reactions. The more endothermic reactions (those which require more energy) are the more temperature dependent reactions. Since the reactions rates are directly proportional to the reactant concentrations, some of the mechanisms can be limited by the available amount of some of the reactants. Its low ionization potential permits its ionization by collisional or other processes much more readily than ionization of the various species of the air or of other materials.

The major mechanisms of sodium ionization are



Certainly not all of these mechanism will be important for all conditions.

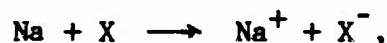
Under some circumstances, there may be only one reaction of importance, while for others there may be a large number. The importance of some of the above mechanisms is definitely limited to certain favorable conditions. Photoionization reactions are unimportant to reentry chemistry.

Collisional ionization,



is the type of reaction which first comes to mind for sodium ionization. It can occur with any species as the collision partner, M. It may be an atom, a molecule, a radical, an ion, or an electron. Certain species are more efficient than others in such reactions*. By far the most efficient is the electron, being more efficient than the larger particles by several orders of magnitude. Thus, in spite of a much lower concentration of electrons than of some atomic or molecular species, the electron can be of importance in collisional ionization. For conditions where the electron density is too low to be of importance in spite of its relatively high efficiency, collisional ionization will primarily occur by collision with atoms and molecules present. The various species of this type have different relative efficiencies for this reaction but there are no data available on such efficiencies. The only available data are for electron collision cross-sections. For the collisional ionization processes, the rate constants can be expected to have an exponential term $e^{-E/RT}$ where the E is the ionization potential, 5.14 e.v. for sodium. Thus, the term for sodium is $e^{-59,700/T}$. The preexponential factor can be obtained for electron collisions from the cross-section data but can only be estimated for other collisions.

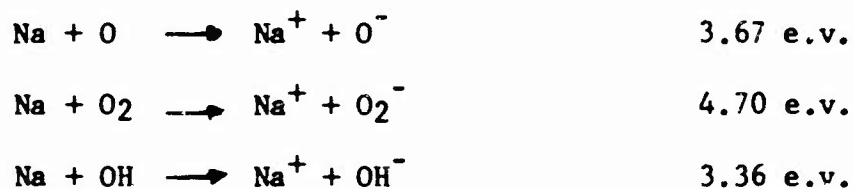
Ion-pair formation,



requires less energy than does collisional ionization for any case where X forms a stable negative ion. The higher the electron affinity of this species,

* Vibrationally excited N_2 is considered on p. 49.

the more stable its negative ion and the less energy required for the ion-pair reaction forming Na^+ . Some of the species which form stable negative ions are the oxygen atom which has an electron affinity of 1.465 e.v., the oxygen molecule which has an electron affinity probably of the order of 0.44 e.v., and the hydroxyl radical which is believed to have an electron affinity of about 1.78 e.v. Other species, such as NO_2 , O_3 , Cl, Br, and F, have even higher electron affinities but are not expected to be present in sufficient concentrations to be important to sodium ionization. The appropriate reactions of the three aforementioned species, together with the energies required for the reactions, are thus



These energies are appreciably less than that for collisional ionization. The exponential terms of the reaction rate constants are therefore not as small. The pre-exponential terms are also expected to be large, that is, the collisional efficiencies are expected to be high, but there are no available data on these reactions and few on any reactions of this type with any species. The lower energy requirements mean that the reactions are not as temperature dependent as collisional ionization reactions and they are probably faster at moderate temperatures. The reaction involving oxygen atoms is probably the most important of these since the species is, for most conditions of interest, present in high concentrations and the reaction requires much less energy than the similar one involving O_2 . That involving hydroxyl radicals depends on their concentration

which can be quite high for some conditions. In such cases, this reaction would be very important.

The negative ions formed in these reactions are, for most conditions, in equilibrium with their neutral species and the free electrons. Thus these reactions do contribute to the electron density even though no free electrons are produced directly in the reactions. They are, instead, produced by rapid detachment from the negative ions, $X^- + M \longrightarrow X + e + M$.

Charge transfer reactions,

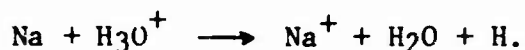


are probably the fastest reactions forming sodium ions for most conditions of interest here. All of the major components of high-temperature air have higher ionization potentials than sodium. The charge transfer reactions with sodium are therefore all exothermic. Since no chemical bonds are broken in this type of reaction, there is probably no appreciable activation energy. The reaction rate constants are probably about as large at low temperature as at high temperature. Thus, unless the temperature is quite high, these reactions will be faster than those previously-discussed ionization reactions which require appreciable energy. Since the most prevalent ion in the high-temperature air is NO^+ , this will be the most important species represented above by X^+ ; but O^+ , N^+ , O_2^+ , N_2^+ and any other ions in the system will undergo this reaction and if present in appreciable concentrations, must also be considered. There is no information on any of these specific rate constants, either on their absolute values or on the values relative to each other. Their

values can thus only be estimated by analogy to other reactions of this type, although such data are also scarce and rather inconclusive.

This reaction can proceed only as long as there are NO^+ ions or other ions to participate in the reaction. If the concentration of such ions is lower than the concentration of free sodium, not all the sodium can be ionized by this mechanism and other mechanisms must ionize the remainder, that is, up to the extent set by equilibrium if such a condition is to be reached. It is also important to note that, although this mechanism differs from the other ionization mechanisms in that it does not form free electrons or other negatively charged particles, it is important to the electron density since it forms a different type ion from those most important in the air system, mainly NO^+ . Na^+ is an atomic ion and, as such, does not recombine with a free electron nearly as readily since it cannot undergo dissociative recombination.

Another charge transfer reaction of a slightly different type is



The H_3O^+ ion is a very prevalent ion in systems with water and this reaction could readily occur in such a system of interest here.

Charge transfer is also possible with other ionic species arising from organic materials. An ion which may be important in this way is CHO^+ .

Associative ionization reaction,



is another mechanism of ionizing sodium with energies less than the ionization potential. The major reaction of this type is that where X represents the water

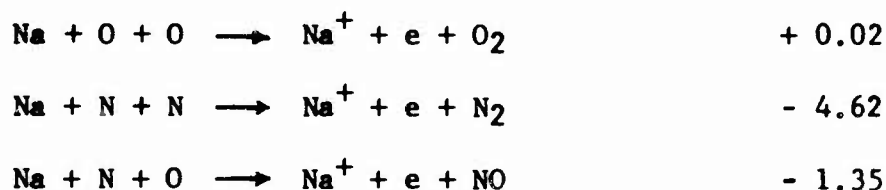
molecule and the resulting ion is therefore $(\text{Na}\cdot\text{H}_2\text{O})^+$. This molecular ion is rather readily dissociated by collision into the sodium ion and water, $(\text{Na}\cdot\text{H}_2\text{O})^+ + \text{M} \longrightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{M}$. This latter reaction is thought to be fast. Evidence in flames indicates this to be an important mechanism. The energy in the first step is of the order of 3 e.v. and is thus considerably below the 5.14 e.v. of collisional ionization. If appreciable amounts of water are present, this reaction is probably important.

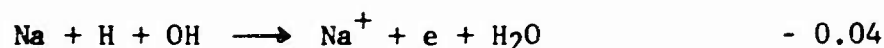
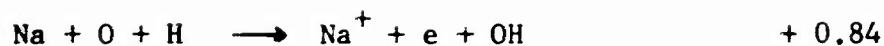
The diatomic ion, Na_2^+ , may be formed by associative ionization. Such would be significant since, being a diatomic rather than atomic ion, it can recombine with an electron at a much faster rate by the dissociative recombination process. However, the process forming Na_2^+ will probably be insignificant unless the sodium concentration is rather high.

The association ionization reactions,



comprise another type of reaction which may occur at low temperatures since they probably require little energy. The X and Y above can represent any prevalent atom or even molecule in the system. While the most prevalent such species is the oxygen atom, others of them, e.g., N, H, OH, are at least as able as the oxygen atom to undergo such reactions. Thus, possible reactions with their energies are





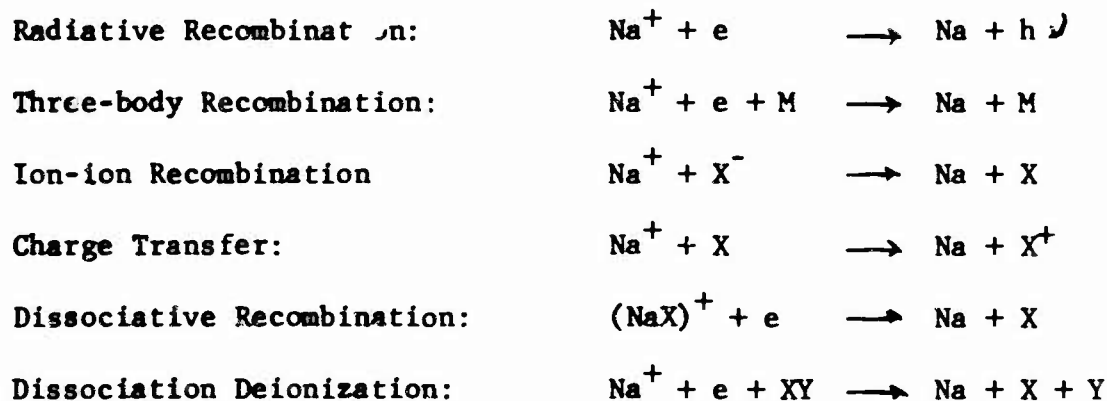
Of these, the two involving nitrogen atoms and that forming water are seen to be exothermic and may require little if any energy. That involving the two oxygen atoms is so slightly endothermic that little energy is required. Of course, there may be some activation energy in which case there would be an exponential term. To settle this, data are needed to get rate constants including temperature dependences. If no appreciable activation energy is required, such reactions may be fast even at low temperatures, providing appreciable amounts of these species are present. That involving two oxygen atoms is most likely to be of importance.

Sodium bonded to other species, e.g. NaO, NaO₂, NaH, have little direct effect on the electron density. Their only appreciable effect is that it causes less sodium to be available in the atomic form for the ionization processes. Thus, if significant amounts of sodium are so tied up, the rate and amount of sodium ionization will be lower.

C. Mechanisms of Deionization

Deionization of sodium involves mainly the reverse of the ionization processes but the energy considerations are considerably different. Practically all of the reactions are exothermic and, hence, have little temperature dependence. Their rates are therefore not limited by small exponential terms but by other considerations of reactants and low collisional efficiencies.

The major mechanisms of sodium deionization are:



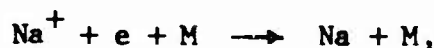
Here also certain mechanisms predominate under some conditions, while others predominate under other conditions. It is to be expected that the first three of these are the most important but the other three cannot be eliminated without further consideration of their possible importance.

Radiative recombination,



is the reverse of photoionization, which is not a significant mechanism of ionization in a flow field. Radiative recombination is not an efficient process but under some conditions (low density, high temperature) may be the fastest of the deionization processes. It can be crudely estimated that only one collision in 10^5 would be effective and more accurate calculations confirm this. The recombination forms neutral sodium atoms in various electronic states with certain of the states being more likely products than others.

Three-body recombination,



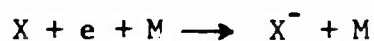
is favored by high densities. Here again, no drastic temperature effects are expected since the reaction is exothermic and no appreciable activation

energy is likely. The relative efficiencies of the various collision partners is the same as for collisional ionization with the electrons being the most efficient and the other possible species having much lower but undetermined efficiencies. Hence, little is known about their rate constants.

Ion-ion recombination, also known as mutual neutralization,



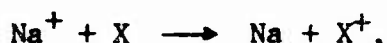
is thought to be a very efficient and, hence, fast process. For many conditions of interest, this will probably be the predominant mechanism of deionization or, at least, will contribute greatly to the overall deionization. The reaction rate constants for this type of reaction are not expected to have any exponential temperature term and thus little temperature dependence. The negative ions required for this type of reaction will mainly be O^- , O_2^- , and OH^- for the reentry conditions, the reactions being the reverse of those given above in the discussion on ion-pair formation. Since the O_2 has a rather low electron affinity, 0.44 e.v., it will not be present in large concentrations and will, therefore, not be as important as O^- and perhaps OH^- . The latter two species have considerably larger electron affinities (1.46 and 1.78 e.v. respectively) and hence are more stable. If the parent species are present in significant concentrations, the negative ions will be important. Since the attachment and detachment reactions



are fast reactions, the negative ions can be expected to be in equilibrium with the parent species and electrons. The concentrations of these negative ions are greater at low temperatures. The ion-ion recombinations are thus

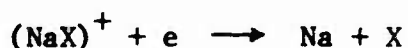
avored by low temperature. They will still be significant at moderate temperatures, however. Little is known about rate constants for ion-ion recombination reactions. Rather rough experimental determinations have been made on a few reactions and approximate theoretical calculations on others. None of these are accurately known and none involve any ions resembling the sodium ion.

Charge transfer reactions,



which neutralize a sodium ion by transferring an electron to it from some other species, are endothermic for all cases of interest, since all major air species have higher ionization potentials. Thus, very little of the sodium, once ionized, will be neutralized by such reactions. The equilibria lie far toward the ionized sodium. These reactions are therefore unlikely to be important.

Dissociative recombination,

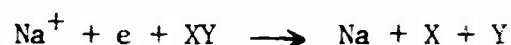


is again a possible reaction with X representing the water molecule. As discussed previously, this ion, $(\text{Na} \cdot \text{H}_2\text{O})^+$, can be formed by the reverse of the above reaction. Its importance depends in part on the amount of water present. This process will compete with the collisional dissociation of the ion. The latter is endothermic, while the dissociative recombination is exothermic. This, however, requires an electron collision, but the ion dissociation can occur with any collision partner. Thus both processes are favored by higher temperatures, the dissociative recombination because of the

greater number of electrons available, and the ion dissociation because of the greater number of collisions with the required energy. No rate constant data are available to determine the relative effects. The rate constants can only be estimated.

No other reactions of this type are likely to be important unless sufficient sodium is present to favor the formation of Na_2^+ which would then readily undergo this type of reaction, i.e., $\text{Na}_2^+ + e \rightarrow \text{Na} + \text{Na}$.

Dissociation deionization,



is exothermic for some cases, endothermic for others, as can be seen from those considered in the reverse reaction. An appreciable activation energy may be involved and even the exothermic reactions may be quite temperature dependent. If any one of these reactions is important, it is most likely to be that where XY represents O_2 . For this to be important, it would require a relatively high density and a high degree of ionization. No rate data are available.

D. The Kinetics of Excitation and Deexcitation

In order to radiate the D-lines, sodium atoms must be in the excited state, 3^2P , which is 2.10 e.v. above the ground state, 3^2S . This state can be reached by any of several mechanisms and atoms can be removed from this state by several mechanisms. The kinetics were discussed briefly above (I. B.). The mechanisms which populate the 3^2P state include

Collisional excitation of ground state Na

Collisional deexcitation of higher excited states

Radiative deexcitation of higher excited states

Deionization of Na^+

Chemi-excitation reactions

Just as in the case of ionization and deionization, the relative importances of the various mechanisms vary with the conditions.

For deexcitation, the reverse of these mechanisms is important

Collisional deexcitation to ground state

Collisional excitation to higher excited states

Ionization

Chemi-deexcitation reactions

and of course the reaction of most interest here

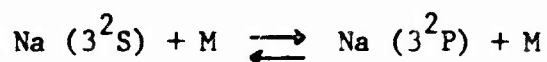
Radiative deexcitation to the ground state

which is the reaction producing the D-lines.

As previously mentioned, the amount of sodium radiation depends on the amount of sodium available in the proper form to radiate. Thus ionized sodium is not available for radiation. If sodium ionization is in equilibrium, this effect on radiation can readily be determined. However, sodium will, for many conditions, take appreciable times to ionize to the equilibrium extent and often will not be able to do so in the available time. Thus, during the time in which sodium is ionized to less than the equilibrium amount, more neutral sodium will be available for radiation than equilibrium will predict. Similarly, the reverse

deionization process is often too slow to follow equilibrium, and once ionized, the concentration of sodium ions will be greater than the equilibrium value. In such cases, the amount of sodium available for radiation is less than would be predicted if the total amount of sodium is considered to be available to radiate. Thus, ionization and deionization kinetics are important to radiation. The intensity of the emission without and including the effect of ionization is shown in Figures 2 and 3. Figure 2 gives the radiation per neutral sodium atom, while Figure 3 gives the radiation per sodium atom, whether neutral or ionized. That is, the radiation in the latter case is reduced by the fraction of ionization. Compound formation would have a similar effect and could be important below 2000°K. The uncertainties in bonding energies and hence in equilibrium constants prevents quantitative consideration of this effect.

Collisional excitation of ground state sodium to the first excited state and collisional deexcitation, "quenching", of that excited state to the ground state,



must be in equilibrium if equilibrium radiation is to be produced. That is, these reactions must be the fastest mechanisms of populating and depopulating the 3^2P state. While this is true for most conditions, there are some conditions for which other mechanisms compete with these. This causes a change from the equilibrium population of the 3^2P state. Different collision partners have different efficiencies in these collisional reactions. Other than electron

collision data, the only known applicable data is for N_2 as a collision partner, and data on the temperature dependence is needed for this. There is, of course, a large temperature dependence of the excitation reaction since it requires 2.10 e.v. for the excitation. There may be other temperature dependence, however. In addition to nitrogen molecules, other species may be important in the collision processes. Some could be much more efficient than N_2 and be important to the rate.

The D-line emission reaction

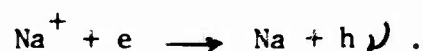


is the reaction most likely to compete with the collisional reactions. It does appear that, for some conditions, it has a significant effect on the overall rate of reexcitation and hence on the 3^2P population. It, therefore, must decrease the radiation. The transition probability of this reaction is well known. The accuracy of D-line radiation intensity calculations depends on the accuracy with which the population of the 3^2P state can be calculated.

Transitions among the various excited states also occur. The available energy levels are shown in Figure 4. Permitted transitions are those between S and P levels, between P and D levels, between D and F levels, between F and G levels, and between G and H levels. These will be by far the most efficient, both for radiative and collisional processes. These are, therefore, the only important transitions. In order for equilibrium to occur, the populations of the various states must be kept in equilibrium by the collisional excitation and deexcitation processes.

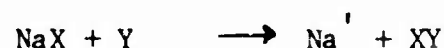
Transitions between the 3^2P states and other excited states of sodium are, of course, also possible. These can be either collisional or radiative. Radiative transitions from the various higher-lying S and D levels to the 3^2P level are permitted transitions and thus have high transition probabilities. Only such radiative transitions are of any importance to the system. Collisional transitions between these same states are also the most likely. In order for equilibrium radiation to occur, the populations of the various states must be kept in equilibrium.

Certain chemical processes tend to form sodium in various excited states. Such excited atoms then tend to deexcite to lower levels often by a cascading process going to progressively lower levels. An example of this type of process is the radiative recombination of Na^+ with electrons



The neutral so formed is often formed in excited states. The states formed in the radiative recombination have been studied. However, while other recombination processes may form neutral sodium in excited states, there is no information on the relative importances of the various states formed. The excited atoms so formed remain excited until they are deexcited by radiative or collisional processes or until they undergo a chemical reaction.

Other chemical reactions can also form or consume excited sodium atoms or can serve to excite or deexcite sodium atoms. That is, chemi-excitation can occur by two general types of reactions



In the first reaction, the energy of the recombination of X and Y will usually be sufficient for the excitation of sodium. The X and Y can represent two atoms, an atom and a free radical, a positive ion or an electron, or any of several other combinations which form a stable bond. The latter reaction may be exothermic or endothermic depending on whether or not the X-Y bond energy is greater than that of the Na-X bond and the sodium excitation energy. Thus the possibility of exciting depends on these bond energies. It is unfortunate that the energies of some of the Na-X bonds are not known with a reasonable accuracy. It is, therefore, not possible to state the energies of some of the reactions, or in some cases, not even whether the reaction is exothermic or endothermic. In such cases, rate constants can not be estimated with any accuracy.

There are no well-established rate constants for any reaction of either of these types of reaction. Estimates have been made for several of the reactions but no real usable data are available.

E. The Kinetics of Sodium Compound Formation

In a system containing sodium, together with such species as O, O₂, H, or OH, compounds can be formed by the sodium. Such compounds can be formed by three-body reactions



or by rearrangement reactions



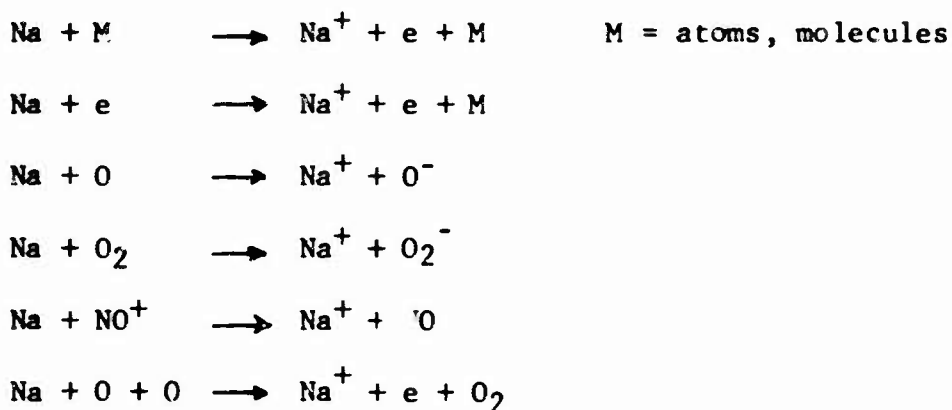
Since, as mentioned above, the bond energies are not well known, especially

for the Na-O and Na-O₂ bonds, neither the kinetics nor the thermodynamics is accurately enough known to determine the importance of sodium compounds. It is to be expected that the compounds will only be important at the lower temperatures of interest, not much above 1000°K. Only approximate statements of this sort can be made, but limits can be placed on concentrations and rates. In this way, the temperature range in which appreciable amounts of sodium can be tied up is somewhat limited.

III. IONIZATION AND DEIONIZATION RATE CALCULATIONS

A. Ionization

With the information described above, rough calculations can be made of the rate of approach to ionization equilibrium. The calculations described here are for a few sets of conditions appropriate to several altitudes in reentry. These were isothermal calculations assuming equilibrium among the air species. The chemical system included what appeared to be the major ionization mechanisms. Our best estimates of the rate constants were used. Specifically, these included the following reactions



The results of early calculations, which used temperatures of 4000-5000°K, are shown in Figure 5. These calculations did not include the ion-pair formation reactions. It is noticed that the times required to approach equilibrium ionization, which for these conditions is nearly the complete ionization of sodium, are quite long. The first ionization of sodium occurred by charge transfer with NO^+ . This reaction slowed up and stopped as the supply of NO^+ was consumed. The next sodium ionization reaction would be that due to electron collision. This appeared to be faster, for most conditions,

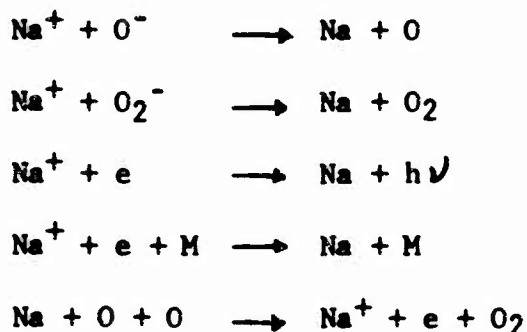
than that due to atom or molecular collision, but errors in rate constants could change the relative importance of these reactions. The electron collision accounts for the second rise in the curves.

However, the later introduction of the ion-pair formation reactions changed the picture. The rates of sodium ionization by the $\text{Na} + \text{O}$ reaction are shown in Figure 6. This is seen to be competitive with, or in general, a little faster than even the charge transfer reaction and is thus the predominant ionization mechanism if the oxygen is dissociated to the equilibrium extent. Even with this reaction included, the ionization does not always reach equilibrium in very short times. For the calculations above 160,000 feet, the amount of sodium ionized in a millisecond is less than the equilibrium amount. Consequently, there would be many more free neutral sodium atoms present and the D-line radiation could be expected to be well above equilibrium. Thus the ionization kinetics are important to the radiation. At the lower temperatures which are sometimes the case, this would be much more pronounced.

These conclusions can only be regarded as qualitative. They are limited mainly by uncertainties in rate constants, by the assumption of equilibrium among the air species, and by the omission of many reactions, including deionization reactions. Since equilibrium may be far from the prevailing condition for many cases, the reactions may have different rates, mostly slower, and may change in relative importance. The uncertainties in rate constants could also cause such changes.

B. Deionization

In a similar manner, rough deionization rates were calculated. Conditions applicable to the lower temperature portion of the wake were used. These would be the most favorable to deionization. These were low temperature isothermal calculations assuming a reasonable set of concentrations of the air species and using our best estimates of rate constants. The chemical system consisted of the following reactions



The reactions, except for one, are all deionization reactions. The last reaction, the association ionization reaction, involving two oxygen atoms, is an ion producing reaction which may require essentially no energy. This reaction may, therefore, occur at any temperature. The chemical system has little temperature dependence. The only reason to consider these calculations as applicable only to lower temperatures is the absence of the endothermic ionization reactions. Since these would only retard the overall deionization process, the slow rates of deionization found by these calculations can really be applied to the entire wake. For this reason, a set of concentrations for the air species applicable to moderate temperatures is quite reasonable. This does make it necessary to consider the major processes changing the concentrations of the air species

while considering the sodium kinetics. For this reason, the rate of the dissociative recombination for NO^+ ,



is compared with the sodium deionization reaction rates.

The results of these calculations are shown in Figures 7 and 8. The deionization rate is obviously slow. For the conditions of these calculations, extremely long times were required for significant sodium deionization. The curves show these rates for two different concentrations (mole fractions) of sodium at each of two altitudes. The three mechanisms of recombination are each found to be important. Ion-ion recombination and three-body recombination at the lower altitude, and ion-ion recombination and radiative recombination at the higher altitude. In addition, it appears that the association ionization reaction could maintain an electron density higher than equilibrium even after the deionization has become appreciable. However, the rate constant for this is so uncertain that such a conclusion is quite tenuous. It should be mentioned that these calculations assumed that sodium was ionized to the equilibrium extent. As was pointed out above in the discussion of ionization rate calculations, this does not appear to be a valid assumption, especially if the amount of sodium is greater than that of NO^+ in the boundary layer. The possibility of continued ionization in the higher temperature regions of the wake makes this less important. However, it is really not important to the times of deionization whether the sodium is fully ionized or only 10% ionized. The latter case is shown by the dotted curve in Figures 7 and 8.

It appears that the slow rate of deionization of a sodium-containing wake would result in a long persistent wake of rather high electron density which decreases, for some altitudes, more by expansion than by chemical processes.

One further point should be mentioned. If sodium is kept at a high degree of ionization, i.e., higher than equilibrium for long times in the wake, there will be less neutral sodium present and, therefore, the radiation intensity will be less than the equilibrium value, especially in the nearer portions of the wake.

While the crudeness of the calculations does not permit quantitative conclusions to be drawn, it seems reasonable that the qualitative results and effects discussed should be expected.

IV. REACTION RATES IN A COMPLETE SYSTEM OF SODIUM CHEMICAL KINETICS

A. The Chemical System and Rate Constants

In order to determine, with as much certainty as possible with our present knowledge, all of the reactions important in sodium kinetics and especially to its radiation and ionization, a very extensive set of reactions was compiled and calculations, as described in the following sections, were made. The chemical system is given in Table I. The system is rather complete and is thought to contain all reactions of sodium of possible importance. It also contains several other reactions not involving sodium. These were included in order to compare their rates with some of sodium and to give a rough idea of the rate at which certain other concentrations were changing. The various photochemical reactions given here (photoionization, photodetachment, photoexcitation and photodissociation) are given for the sake of completeness and were not used in these calculations since their rates would not be very significant. Of course, if this system were used to study the normal atmosphere, such reactions would have to be included.

For most of the conditions, such species as O^- , O_2^- , Na^- and Na_2^+ were assumed to be in equilibrium with their parent species.

Each reaction involving free neutral sodium involves not only the ground state atoms (3^2S) but also the various excited states. The four states, (3^2S , 3^2P , 4^2S , and 4^2P) were specifically included herein. These are listed individually in certain of the reactions. However, in those where no specific state is mentioned, each of these four was considered

individually. Thus the rate of formation or consumption of atoms in each of these states by each of the reactions was considered. Other sodium states were not specifically considered since they are less important for this study.

Each reaction listed is followed by the energy of the reaction (in e.v.), a positive value indicating the energy consumed by the reaction. The rate constants used are given next by the values of a, b, and c, which represent the rate constants by the form

$$k = a T^b e^{-c/T}$$

The value of a is given as a constant, in units such that concentrations are in particles cm^{-3} , followed, in parentheses, by the power of ten by which the constant is multiplied. That is, 5 (-8) means 5×10^{-8} . The value of c given is in units of $^{\circ}\text{K}$. A rate constant of $5 \times 10^{-8} T^{1/2} e^{-10,000/T}$ would be given by 5 (-8), 0.5, and 10,000 in the a, b, and c columns respectively. The same data have been given for the reverse reactions in the columns headed a', b', and c'.

Where published data on rate constants are available, the references are given following the reaction. These may be experimental, theoretical or analytical data. These were considered but not necessarily used for the rate constants of the referenced reactions. If, as in most cases, no data were available, estimates were made for reasonable values of the rate constants. These were, in general, based on knowledge of other reactions of the same type. A discussion of many such reactions has been given elsewhere.^{1,2} The rate constants for the most important reactions are discussed in detail later.

B. Calculation of Instantaneous Rates

The rates of the reactions listed above have been calculated for a number of sets of conditions appropriate to reentry boundary layers and wakes. These calculated the instantaneous rates of the reactions for specific conditions and did not attempt to calculate the temporal change of concentrations which would require the coupling of gas dynamics effects or introduce further uncertainties. The rates thus calculated depend only on the concentrations of the species and on the reaction rate constants used. The uncertainties result only from these quantities.

These calculations were designed to determine the relative importances of the various reactions to sodium chemical kinetics and effects. In this way, all of the reactions which should be included in non-equilibrium sodium calculations can be found. Thus recommendations for the chemical kinetics to be coupled with gas dynamics calculations can be made.

The conditions used were those appropriate to boundary layer and wake for several altitudes in reentry. They are given in Table II. They were chosen to show effects of altitude, temperature, density, wake distance, and variation from equilibrium. These few sets of conditions were not sufficient to completely show all of these effects but, at least, gave some ideas of the effects and can tell which reactions are of importance.

C. Reactions Controlling Concentrations

Having calculated the rates of the many reactions involving the various forms in which sodium can occur, the reactions which control the concentrations

of each of them can be found. The following tables list, for each of the several sets of conditions, the reactions which most rapidly form and consume each of the various species. In Table III, the reactions important to Na^+ are given, while those important to free electrons and excited sodium, $\text{Na}(3^2\text{P})$ are given in Tables IV and V respectively.

These rates will fix the concentrations only if there is sufficient time. Thus, from the total rate of reactions involving any certain species and the available reaction time, an idea can be obtained of the likelihood of reaching near-equilibrium concentrations.

The data given in Table III show definitely that ion-pair formation dominates the production of sodium ions. For all conditions with temperatures of 2000°K and above, these reactions are much faster than any others forming Na^+ . Of greatest importance is the reaction



This is quite significant since this has not been the usually assumed mechanism for sodium ionization. Although these calculations were made for typical wake conditions, it seems evident that the range of conditions used suffice to show that it is also true for boundary layer conditions. It was this result that suggested the inclusion of this reaction in the ionization calculations presented in Chapter III.

The extent of the predominance is such that this reaction will predominate even if the rate constants are at the extreme limits which least favor this reaction.

The other reaction which competes with the above reaction is the similar reaction involving OH,



The possible importance of this reaction depends on the OH concentration.

The assumed values of this concentration were only values which are reasonable but, of course, these could vary drastically. It would not become as important as the other ion-pair formation reaction unless the OH concentration were extremely high or unless the oxygen atom concentration were much below equilibrium.

The ion-pair formation reaction involving O_2 is not as important as the above since its concentration is lower and its rate constant is lower.

The charge transfer reaction with NO^+ will be important where appreciable amounts of NO^+ are present. The assumptions of this study included earlier consumption of the NO^+ by this reaction and a resulting low NO^+ concentration in the wake.

Other types of ionization mechanisms are evidently of less importance. The associative ionization involving the hydrated sodium ion, $(\text{Na} \cdot \text{H}_2\text{O})^+$ appears to be of importance in some cases. However, the production of this ion is not rapid and it does not appear that this reaction will be important unless much higher amounts of water are present. In these calculations, assumed water concentrations were in the range of 10^{-11} to 10^{-4} of the total.

The three-body ionization, herein called association ionization, appears to be of limited importance. Under some of the lower temperature conditions, this approaches the rates of the ion-pair formation reactions. At still lower

temperatures, that is, below 1000°K, this would probably dominate the sodium ionization, especially if the atomic oxygen were present in greater-than equilibrium concentrations as is quite possible. The calculations made here at 1000°K (H and I) assumed the low equilibrium concentrations of atomic oxygen.

The collisional ionization of sodium, which is the usually accepted mechanism, is found here to be of little importance. Where such a reaction does appear to be fast enough to be within a few orders of magnitude of the fastest reactions, it is that with the electron as the collision partner which contributes. Ionization by collision with atoms or molecules is too slow to be important. If conditions arise where the temperature is fairly high but there is very little oxygen dissociation, collisional ionization could be more important.

The relative rates of the sodium ionization reactions do not depend on the absolute sodium concentration since their absolute values are all directly proportional to it.

The production of free electrons (Table IV) is largely controlled by the same processes that control sodium ion production. The ion-pair formation producing Na^+ , which also produces negative ions, mainly O^- , can be thought of as producing negatively charged particles. For practically all conditions of interest, the negative ions (O^- , O_2^- , OH^-) are in equilibrium with free electrons. Hence, the negative ion formed by the ion-pair formation reaction quickly undergoes a collisional detachment reaction producing a free electron,

$X^- + M \longrightarrow X + e + M$. Thus the ion-pair formation can be thought of as producing a free electron and thus is the indirect reaction supplying free electrons, although the detachment reactions appear to control the electron density.

The other types of reactions, associative ionization, association ionization, and collisional ionization, are all of minor importance. The comments concerning these reactions made in the discussion of sodium ionization apply here as well.

The deionization of sodium (Table III) occurs primarily by three types of reaction, radiative recombination, three-body recombination, and ion-ion recombination. The last is the reverse of ion-pair formation which accounts for much of the ionization. The ion-ion recombination is that of Na^+ mainly with O^- but somewhat with OH^- and with O_2^- . The reaction with OH^- depends on the OH concentrations which in these calculations were taken between 10^{-6} and 10^{-3} of the total. Radiative recombination, $Na^+ + e \longrightarrow Na + h\nu$, is the reverse of photoionization which was not considered in the ionization mechanism. In this reaction, the neutral sodium atoms are formed in many different electronic states, some being more favored than others. This is true of any deionization reaction in which there is sufficient energy but in this case, there are no other particles to share the energy. This reaction is favored by high temperatures, since this reduces the number of negative ions which can undergo ion-ion recombination, and by high altitudes, since this limits the number of three-body collisions. Three-body recombination is favored by low altitudes. It is the reverse of collisional ionization

and the third-body can be any other particle, the electron having by far the highest efficiency. The diatomic sodium ion, Na_2^+ has no appreciable effect on the electron density.

The free electron consuming reactions (Table IV) are about the same as the sodium deionization except that the ion-ion recombination does not directly remove electrons but depends upon the formation of negative ions by attachment reactions which are the fastest electron removing reactions but are nearly in equilibrium with the detachment reactions. The attachment-detachment reactions thus have no net effect on the electron density. The electron density depends rather on the formation and destruction of negative ions by the ion-pair formation and ion-ion recombination, or on other electron forming and removing reactions. That is, when detachment from O^- controls the electron density, it is really the $\text{Na} + \text{O} \rightleftharpoons \text{Na}^+ + \text{O}^-$ reaction which controls it indirectly. The exception to this is under conditions for which radiative attachment is competitive with three-body attachment. This sets up a steady state situation between the negative ions and electrons. Here they are not in equilibrium but the steady state acts similarly and has no net effect on the electron density.

The total rates of ionization and of deionization are, in general, not equal since ionization equilibrium was not the condition assumed.

The data in Table V give the kinetics of excited sodium, $\text{Na} (3^2\text{P})$, and hence of D-line radiation. It is immediately evident from these data that the population of this state is not controlled by its collisional excitation and deexcitation. The radiative deexcitation, for equilibrium conditions,

is considerably faster than collisional deexcitation. Thus the population of this state will be reduced until a steady-state condition is reached. For all cases run for altitudes of 100,000 ft. and greater, the radiative deexcitation is from 10 to 100 times faster than the collisional process. The population of the excited state and hence the radiation will, therefore, be from 10 to 100 times lower than equilibrium radiation for the given sodium concentrations. For the one condition at 60,000 ft., the rates are competitive and the radiation would be expected to be reduced only by about 40%. Such non-equilibrium among the electronic states and the resulting effect on radiation is known as "collision limiting"; that is, the relative populations are not those given by the equilibrium constant. This appears to be an important consideration.

An examination of Table V shows some chemi-excitation and chemi-deexcitation reactions which make some contribution. These, however, are, in general, at least two orders of magnitude slower than the competing processes and uncertainties in these are expected to be towards slower rather than faster rates. It is to be noted, however, that for the condition (H) which is for a low temperature situation with a higher degree of ionization, as will often be the case in a sodium wake, a chemi-excitation reaction is the fastest process populating the Na (3^2P) level. Its rate is even greater than the rate of radiative deexcitation. The population of this state should thus increase and the radiation should be greater than predicted by equilibrium distribution among the electronic states. There should be some tendency for this in any situation where the sodium is ionized to more than the equilibrium extent, but such a tendency will not always have any appreciable effect.

If higher states are populated to a greater-than-equilibrium extent, these can be important in the Na (3^2P) kinetics as in case I. However, this is not too likely a condition.

It should be remembered that the sodium radiation is dependent not only on the kinetics directly exciting and deexciting sodium but also on any which affect the total amount of sodium present as free neutral atoms. That is, sodium present as the ion or bound in a molecule can not contribute to the D-line radiation and the kinetics affecting such species must also be important to radiation.

Sodium compound formation becomes important (for conditions applicable to 150,000 ft.) at temperatures between 1000 and 2000°K. While NaO does not appear to be of any great importance, NaO₂ is. This is because at the low temperatures for which the equilibrium favors compound formation, the equilibrium O₂ concentration used was much greater than the atomic oxygen concentration. Of the reactions forming compounds, only those forming NaO₂ appear to be fast enough to form appreciable amounts in the available time. Of course, the Na-O and Na-O₂ bond energies are not well known so the steady-state NaO and NaO₂ concentrations may be badly in error. The calculations made here indicate that, for one set of conditions at 2000°K, no sodium compound is of much importance, that is, the amount of sodium bound in compounds is not an appreciable part of the total. However, at 1000°, the equilibrium between Na and NaO₂ greatly favors the NaO₂ and the reactions forming it are fast enough to form considerable amounts of it in a matter of milliseconds. There may not be time in some cases, however, to reach near-

equilibrium concentrations of NaO_2 . These rough calculations give the following values for the ratios of the steady-state concentrations

| | 1000°K | 2000°K |
|------------------------------|--------|--------|
| $(\text{NaO})/(\text{Na})$ | .02 | .0001 |
| $(\text{NaO}_2)/(\text{Na})$ | 500 | .02 |

The importance of NaO_2 at temperatures below 2000°K is obviously great. Since so much of the sodium will be bound up at temperatures of the order of 1000°K, there will be little free neutral sodium and, hence, much less radiation than if none were in the form of compounds. At lower altitudes, this would be more pronounced since the three-body reaction forming NaO_2 is extremely density dependent.

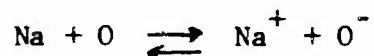
In the computations made, many parameters were varied. Among these were the effect of altitude, temperature, density, rate constant uncertainties, and non-equilibrium concentration of various species. In the small number of calculations, the quantitative effect of each parameter could not be determined, but a number of qualitative and semi-quantitative effects could be seen. These have, in general, been mentioned above in the individual discussions of the Na^+ , electron, Na (3^2P), and sodium compound kinetics. The effect of uncertainties in rate constants can best be seen by considering the rates of the specific individual reactions and figuring the effect on the species involved of changing the rate constant. The effect which is least clear is that of non-equilibrium concentrations since there are so many possible variations. Only a few were considered here. Another effect which is important is that of organic materials. The quantities of these and

resulting species present and the degree of non-equilibrium among these is seen to be very important.

V. CONCLUSIONS AND RECOMMENDATIONS FOR SODIUM KINETICS

A. Conclusions

These calculations have shown that the reaction

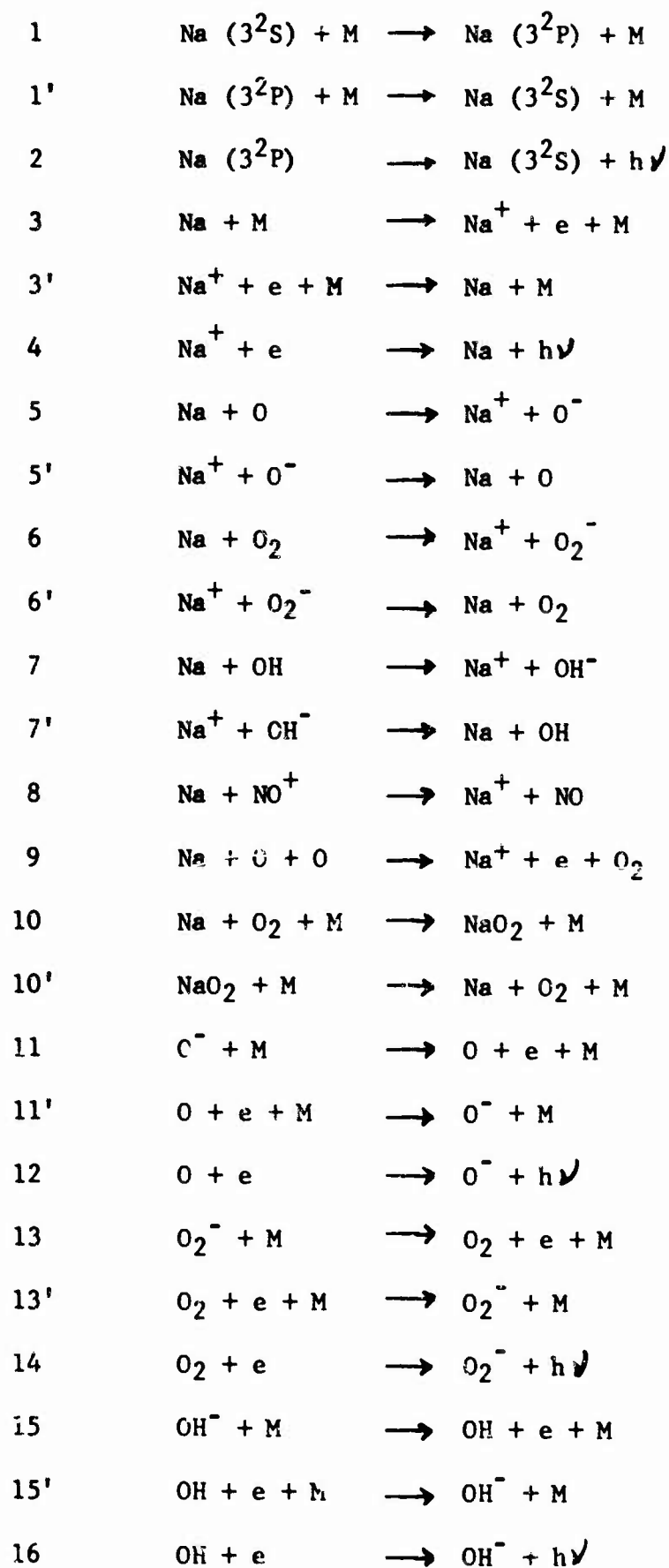


is extremely important to the chemical kinetics of ionization and deionization (and hence to electron density) as well as to sodium radiation. While, as discussed in detail above, other reactions make important contributions to the electron densities, depending on the conditions, the above reaction is of greatest importance. These calculations also show the occurrence of collision limiting (non-equilibrium excitation) in the case of the sodium D-line radiation. For some conditions, the radiative deexcitation of Na (3^2P) is as much as 100 times as fast as the collisional deexcitation and the radiation is correspondingly reduced. The importance of ionization non-equilibrium to the radiation has also been shown.

A system of sodium chemical kinetics, recommended for use in any non-equilibrium flow field calculations involving sodium, is given in the next two sections.

B. The Chemical System

The chemical system, which should be used in non-equilibrium calculations, is dependent on the intent of the calculations. Those interested in radiation will not need exactly the same system as those concerned with ionization and so on. On the other hand, they are not entirely separable. The following system is designed to include all of the reactions most important to any of the effects of sodium.



Reactions 1 and 2 largely control the sodium radiation for any given free neutral sodium concentration. M may be any collision partner.

Reaction 3 will be important only at high temperature while its reverse reaction, 3', is important at low altitudes. M may be any collision partner, electrons being the most efficient. Reaction 4 is important at high altitudes.

Reactions 5 and 5' are of great importance to ionization. Reactions 6 and 6' are of less importance but may be needed where O_2 is dissociated to much less than the equilibrium extent. Reactions 7 and 7' depend on the amount of OH present.

Reaction 8 is important where appreciable amounts of NO^+ are present. The reverse reaction should be unimportant. The importance of reaction 9 is uncertain. Its reverse should be unimportant.

Reactions 10 and 10' are important at temperatures below $2000^\circ K$ since they cause much of the sodium to be tied up in compounds.

The remaining reactions are for many conditions in equilibrium. For some conditions, particularly at low temperatures or low densities, this may not be so. The radiative reaction may compete with the collision reaction. For calculations this must be considered and either equilibrium assumed or the rates calculated depending on the conditions. The reactions involving O^- (11 and 12), O_2^- (13 and 14), and OH^- (15 and 16) are important when the corresponding reactions (5, 6, and 7 respectively) are important.

For many conditions, reaction 5 completely accounts for the ionization. In such a case, however, reactions 11 and 12 must be included, sometimes in

equilibrium. Deionization is usually more complex, often requiring reactions 3 and 4 in the kinetics. Radiation is largely accounted for by reactions 1 and 2, although some of the other reactions (ionization and compound formation) may be needed to determine the concentration of free neutral sodium atoms.

C. The Reaction Rate Constants

The values of the reaction rate constants recommended for use in this chemical system are

| <u>Reaction</u> | <u>k</u> |
|-----------------|---|
| 1 | $6 \times 10^{-10} e^{-24,700/T}$ or $3 \times 10^{-8} T^{1/2} e^{-24,400/T}$ for M = electron |
| 1' | 2×10^{-10} or $1 \times 10^{-8} T^{1/2}$ for M = electron |
| 2 | 6.25×10^{-7} |
| 3 | $6.5 \times 10^{-18} T^{3/2} e^{-59,700/T}$ or $6.5 \times 10^{-10} T^{1/2} e^{-59,700/T}$ for M = electron |
| 3' | 2.7×10^{-33} or $2.7 \times 10^{-25} T^{-1}$ for M = electron |
| 4 | $2.0 \times 10^{-10} T^{-.75}$ |
| 5 | $3.3 \times 10^{-9} e^{-43,000/T}$ |
| 5' | $2 \times 10^{-7} T^{-1/2}$ |
| 6 | $3 \times 10^{-9} e^{-54,500/T}$ |
| 6' | $2 \times 10^{-7} T^{-1/2}$ |
| 7 | $3 \times 10^{-9} e^{-35,000/T}$ |
| 7' | $1 \times 10^{-7} T^{-1/2}$ |
| 8 | $5 \times 10^{-11} T^{-1/2}$ |
| 9 | $1 \times 10^{-32} e^{-230/T}$ |
| 10 | 1×10^{-30} |
| 10' | $1 \times 10^{-9} e^{-20,000/T}$ |

| <u>Reaction</u> | <u>k</u> | |
|-----------------|-------------------------------------|--------------------|
| 11 | $1 \times 10^{-11} T e^{-17,000/T}$ | M = O ₂ |
| | $3 \times 10^{-13} T e^{-17,000/T}$ | M = N ₂ |
| 11' | $1 \times 10^{-27} T^{-1/2}$ | M = O ₂ |
| | $3 \times 10^{-29} T^{-1/2}$ | M = N ₂ |
| 12 | 1.2×10^{-15} | |
| 13 | $5 \times 10^{-13} T e^{-5,100/T}$ | |
| 13' | $1 \times 10^{-28} T^{-1/2}$ | |
| 14 | 1×10^{-18} | |
| 15 | $1 \times 10^{-12} e^{-24,500/T}$ | |
| 15' | $1 \times 10^{-28} T^{-1/2}$ | |
| 16 | 1×10^{-15} | |

A general idea of the state of knowledge of rate constants has been given previously for the complete system of reactions or for types of reactions. Having reduced the system to 23 reactions, the rate constants can now be discussed specifically.

For reaction 1, the only directly applicable data are for electron collisions. These data^{3,4,5,6} of the cross-section as a function of energy can be used to directly obtain a rate constant with temperature dependence. For the reverse process, reaction 1', the only applicable data are for the case of N₂ as a collision partner. These data^{7,8} have been reviewed⁹ in some detail. The rate constant of reaction 1 for this collision partner can be obtained by applying the equilibrium constant. This is a correct procedure for the case of such an atomic electronic transition. Likewise, for the above-mentioned

electron collisional excitation data, the rate constant for the deexcitation can be obtained by use of the equilibrium constant. The major problems for this reaction are the temperature dependence for the N_2 collision process, and the relative efficiencies for other collision partners. The only other data are for H_2 and CO as collision partners and nothing is available for such collision partners as O_2 , N , O , NO or any other minor constituent.

For the rate of reaction two, the well-known transition probability of the sodium D-lines is simply a first-order rate constant.

For reaction 3, data are available only for the case of the free electron as a collision partner. The data which are for the cross section as a function of energy can be used to obtain a rate constant and its temperature dependence.

By considering the relative cross section data of Tate and Smith¹⁰, of Kaneko¹¹, and of Brink¹², and the absolute cross section data of Brink¹³, the composite cross section curve as a function of energy shown in Figure 9 was obtained. From the data of this curve, a rate constant expression was obtained for a system with a Boltzmann energy distribution. The rate constant so obtained is that given in the foregoing table.

From this and the equilibrium constant, that of the reverse reaction, 3', can be obtained, but since the various electronic states are not necessarily in equilibrium, such may not be entirely correct. For other collision partners, it is necessary to assume a collision efficiency, relative to that of the electron. Since electrons travel faster than atoms or molecules, they undergo more collisions. It is also known that the transfer of energy in such a collision is much more

likely. Thus the electron collision will have a much higher rate constant than a collision of an atom or molecule. The relative value is probably of the order of 10^4 to 10^5 . The only systems for which such data are known to be available are those of N_2 and O_2 ionization. Data are available for N_2 ionization by electron collisions^{14,15} and by N_2 - N_2 collisions¹⁶ and for O_2 ionization by electron collisions^{14,15,17,18} and by O_2 - O_2 ¹⁹ and O_2 - N_2 ¹⁹ collisions. The data for these systems have relative rate constants of the order of magnitude mentioned above. These are, of course, considerably different from the sodium system and the relative values of rate constants may be considerably different. The rate constant for reaction 4 has been calculated by Bates.²⁰

No rate data are available for reactions 5, 6 and 7 nor for any reactions of the type of the forward reactions. Neither are there data for the specific reverse reactions of these. The only related data are for ion-ion recombinations of other systems, none of which involve sodium.^{21,22,23,24,25,26} These data indicate rate constants in the range of 10^{-8} - 10^{-7} $\text{cm}^3 \text{ sec}^{-1}$ with the temperature dependence estimated as $T^{-\frac{1}{2}}$. It has thus been assumed that the rate constants of the reactions of interest here, 5', 6' and 7', are in this range. The rate constants for the forward reactions were obtained by use of these and the equilibrium constants, the use of which has the limitations previously mentioned.

For reaction 8, there are no data. The rate constant recommended here is in the range of those for such charge transfer reactions, assuming there is no activation energy.

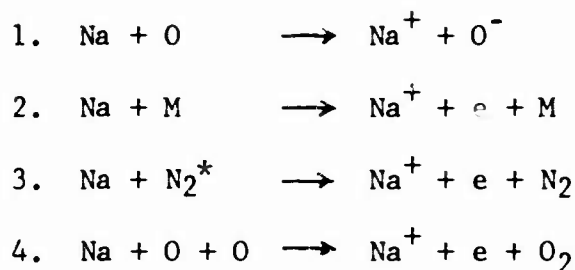
For reaction 9, there are no data. The only data available are for the reaction involving cesium and nitrogen atoms.²⁷ There is some question as to the mechanism in the study by which those data were obtained and the resulting rate constant is therefore in considerable doubt. The rate constant for reaction 9 is thus extremely uncertain, perhaps the most so of any of the reactions considered here.

Reaction 10' has been studied and some rate data obtained, presumably for the three-body reaction.^{28,29} These data are not very accurate but appear reasonable. However, since the energy of the Na-O₂ bond is not well known, the equilibrium constant is not accurately known. Thus the rate constant for the reverse reaction, the NaO₂ dissociation, is quite uncertain.

The attachment and detachment processes have been discussed elsewhere^{2,30} in detail. The rate constant for the radiative attachment to atomic oxygen is accurately known but that for molecular oxygen is somewhat uncertain but certainly lower. The results of studies are dependent on the value of the electron affinity which is not definitely established. For collisional attachment and detachment, there is appreciable uncertainty in the rate constant for atomic oxygen, while those for O₂ are rather well established. There is no information on OH⁻ and the rate constants were only taken by analogy to other such reactions using the latest value for the electron affinity, 1.78 e.v., which is not definitely established.

D. Some Considerations of Relative Ionization Rates

It may be informative to compare the relative rates of certain ionizing reactions in terms of the factors which determine them. Consider the four reactions



The rates of these are given by

$$\begin{aligned}
 v_1 &= k_1 (\text{Na}) (\text{O}) = a_1 e^{-(I-A)/kT} (\text{Na}) (\text{O}) \\
 v_2 &= k_2 (\text{Na}) (\text{M}) = a_2 e^{-I/kT} (\text{Na}) (\text{M}) \\
 v_3 &= k_3 (\text{Na}) (\text{N}_2^*) = a_3 e^{-(I-V)/kT} (\text{Na}) (\text{N}_2) e^{-V/kT} = a_3 e^{-I/kT} (\text{Na}) (\text{N}_2) \\
 v_4 &= k_4 (\text{Na}) (\text{O})^2 = a_4 e^{-E/kT} (\text{Na}) (\text{O})^2
 \end{aligned}$$

where

I = ionization potential of sodium = 5.14 e.v.

A = electron affinity of atomic oxygen = 1.46 e.v.

V = energy of the vibrational state of N_2^*

E = activation energy of reaction 4

The pre-exponential factors, a_i , which are indications of relative collision efficiencies, vary considerably. That for reaction 3 is very low. That for reaction 2 has been estimated to be four orders of magnitude higher than that of reaction 3. However, this is probably still lower than that of reaction 1. The relative rates of 1 and 3 are

$$\frac{v_1}{v_3} = \frac{a_1}{a_3} e^{17,000/T} \frac{(\text{O})}{(\text{N}_2)}.$$

At temperatures of interest, the exponential factor is of the order of several hundred, and a_1 is at least as large as a_3 . Thus, unless the atomic oxygen is less than a hundredth of its equilibrium value, reaction 1 will be the faster.

Such a departure from equilibrium is not expected at conditions of interest to sodium boundary layer ionization.

The relative rates of 1 and 4 are not as simple to compare. Calculations discussed in Section IV have indicated that 1 should be much faster. The ratio of their rates is

$$\frac{v_1}{v_4} = \frac{a_1}{a_4(0)} e^{-(I-E)/kT}$$

The exponential term is more favorable to reaction 4 at low temperatures. However, if the atomic oxygen concentration is anywhere near the equilibrium value, it is very low for low temperatures. The most likely case for 4 to be important is for far wake conditions with the atomic oxygen concentration higher than equilibrium. This would appear to be the only condition where 4 could be important. It should be mentioned that the activation energy of 4 may be essentially zero but is more likely to be appreciable and would make this reaction slow under any conditions.

Reaction 1 requires the detachment from negative atomic oxygen ions to be important. This will certainly be so if ionization reactions are fast enough to have any importance. For most conditions, these ions will be in a steady state condition with electrons.

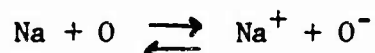
These considerations show the probable primary importance of the ion-pair formation in sodium ionization.

E. Directions for Further Study

Although certain conclusions can be definitely drawn from this study, it is obvious that much more work is needed both of an analytic nature and experimental.

Until better data on some rate constants are available, it would be wasteful to do great numbers of calculations. However, a limited number of further calculations similar to those described herein seem justified. These should be done in order to better separate the many parameters which could be tested to show the effects of altitude, temperature, density, non-equilibrium, compound formation, ionization, excitation, etc. Particularly needed are some calculations with different degrees of sodium ionization. It would also be informative to use this system to make calculations on the normal atmosphere.

The major need is for experimental data. Uppermost on this list is for data to obtain a rate constant for the reaction



as well as for other reactions of this type. Since the reaction is, for many conditions, the most important in both ionization and deionization, rate constants are badly needed and good experimental programs are needed to obtain these data. Data for collisional ionization with various collision partners, for collisional excitation and deexcitation with various collision partners, for the charge transfer reaction and for the association ionization reaction are needed. That is, data is needed most for reaction 5 and then also for reactions 1, 3, 8, 9, 7, and 6. These must include temperature dependence data. Until these data are available, no reliable calculations of flow field sodium radiation or electron density can be made and only general qualitative conclusions can be found.

ACKNOWLEDGMENTS

The author appreciates the interest and helpful suggestions of Dr. W. E. Kaskan, as well as the interest of a number of colleagues. He would also like to thank Mrs. Patricia Brazel for her important work on the calculations described herein.

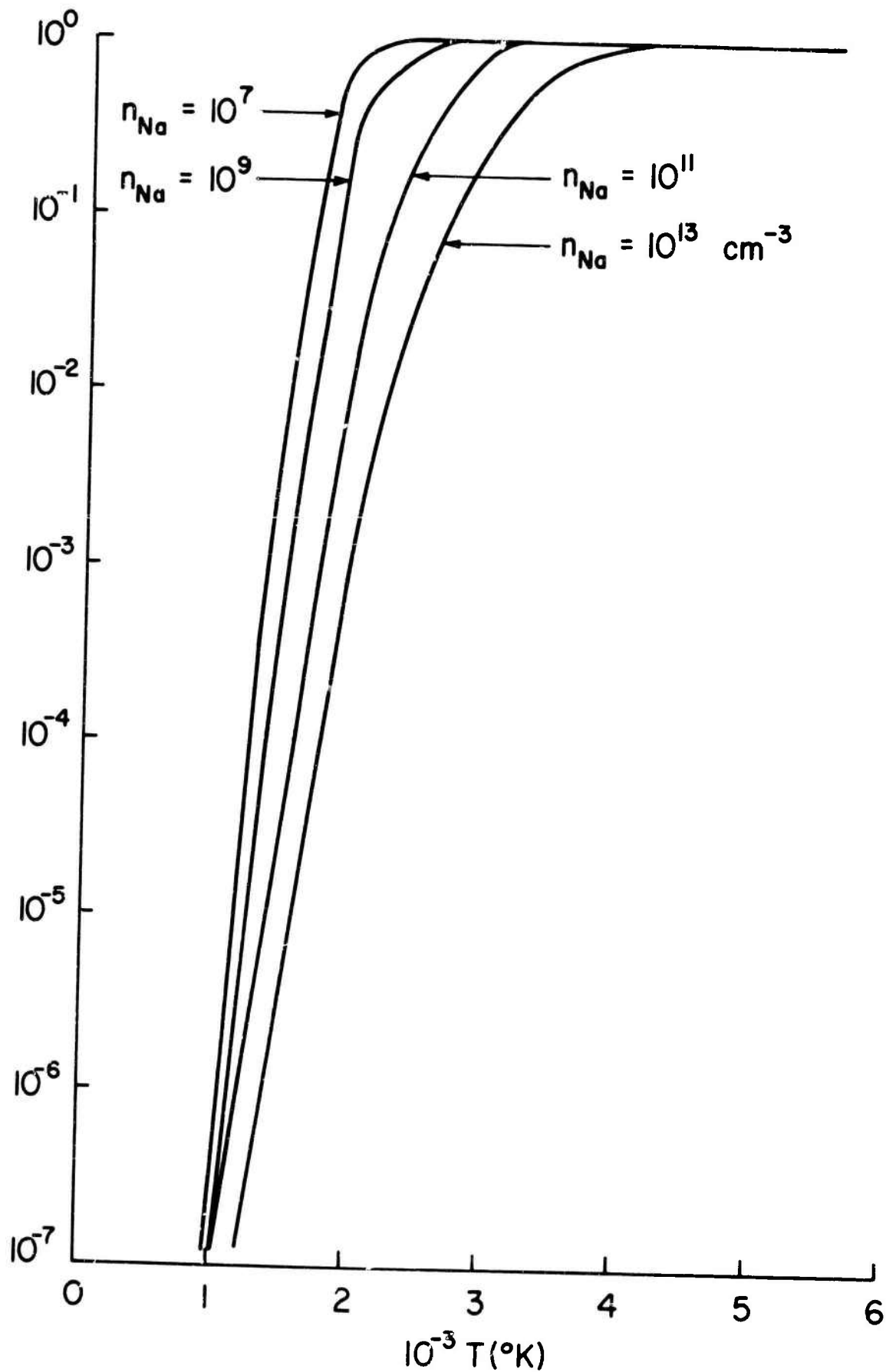


Figure 1. Fraction of Sodium Ionized at Equilibrium for Various Sodium Concentrations

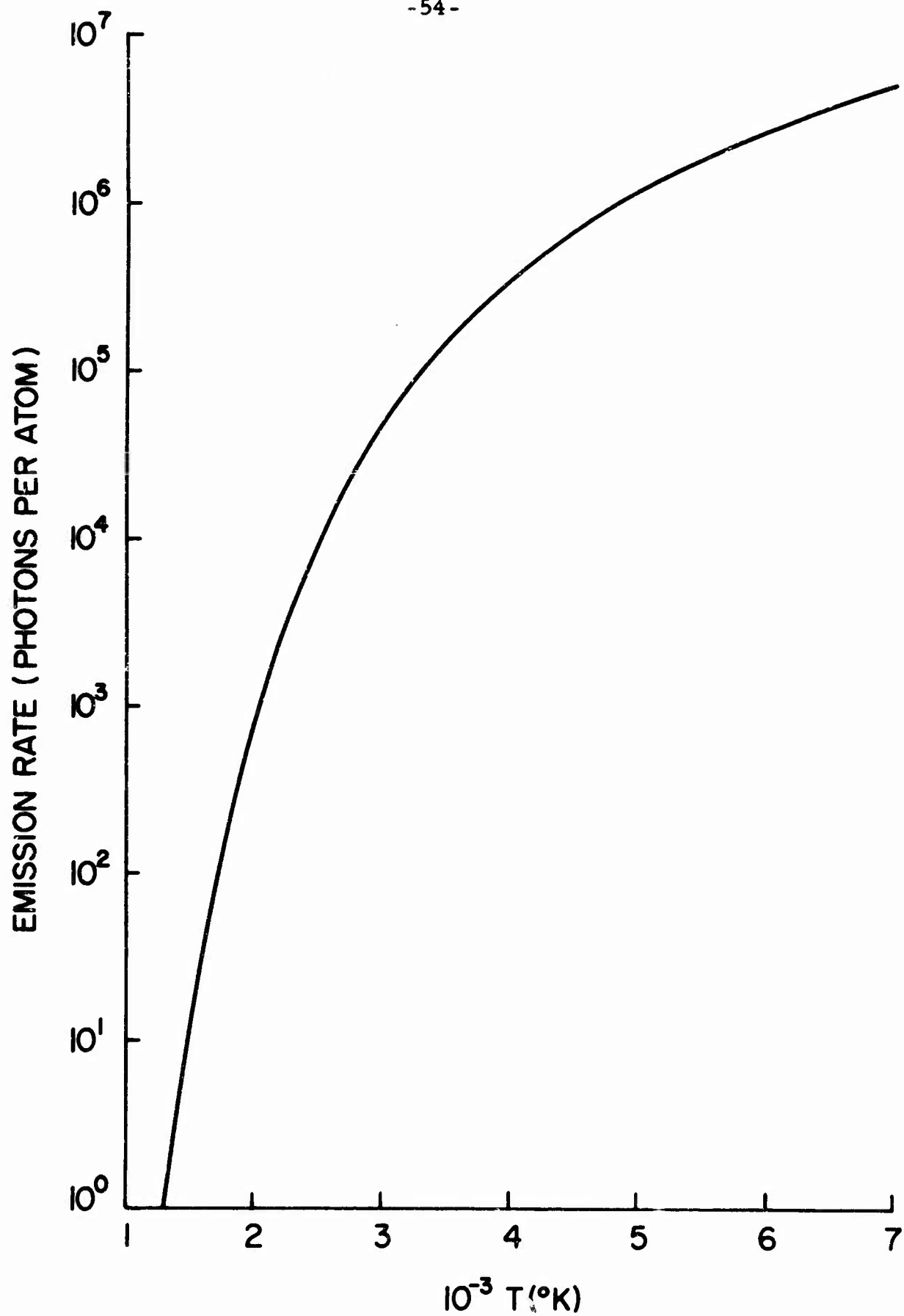


Figure 2. Rate of Sodium Emission per Neutral Sodium Atom

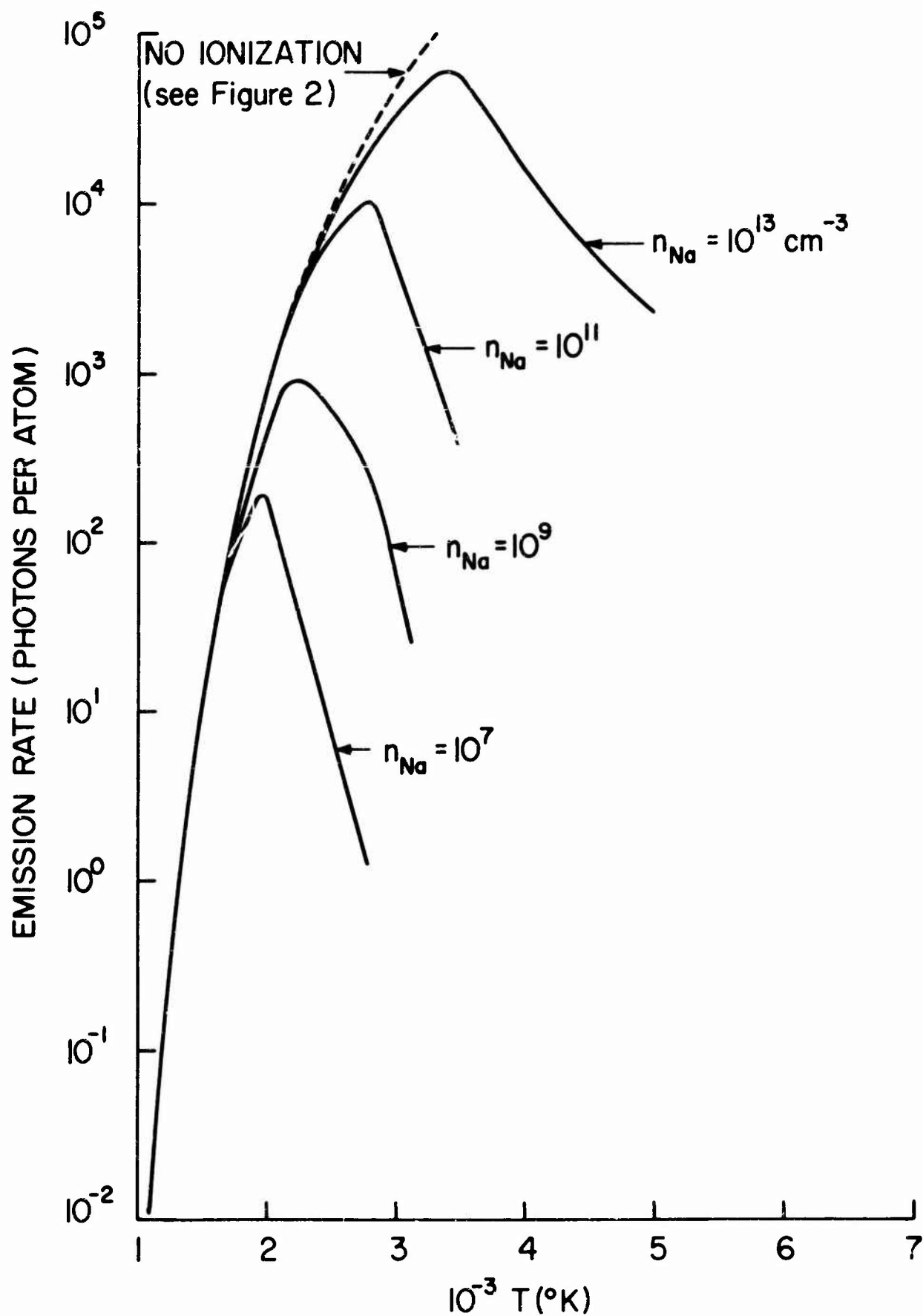


Figure 3. Rate of Sodium Emission per Sodium Atom (neutral or ionized) for Various Concentrations of Total Sodium

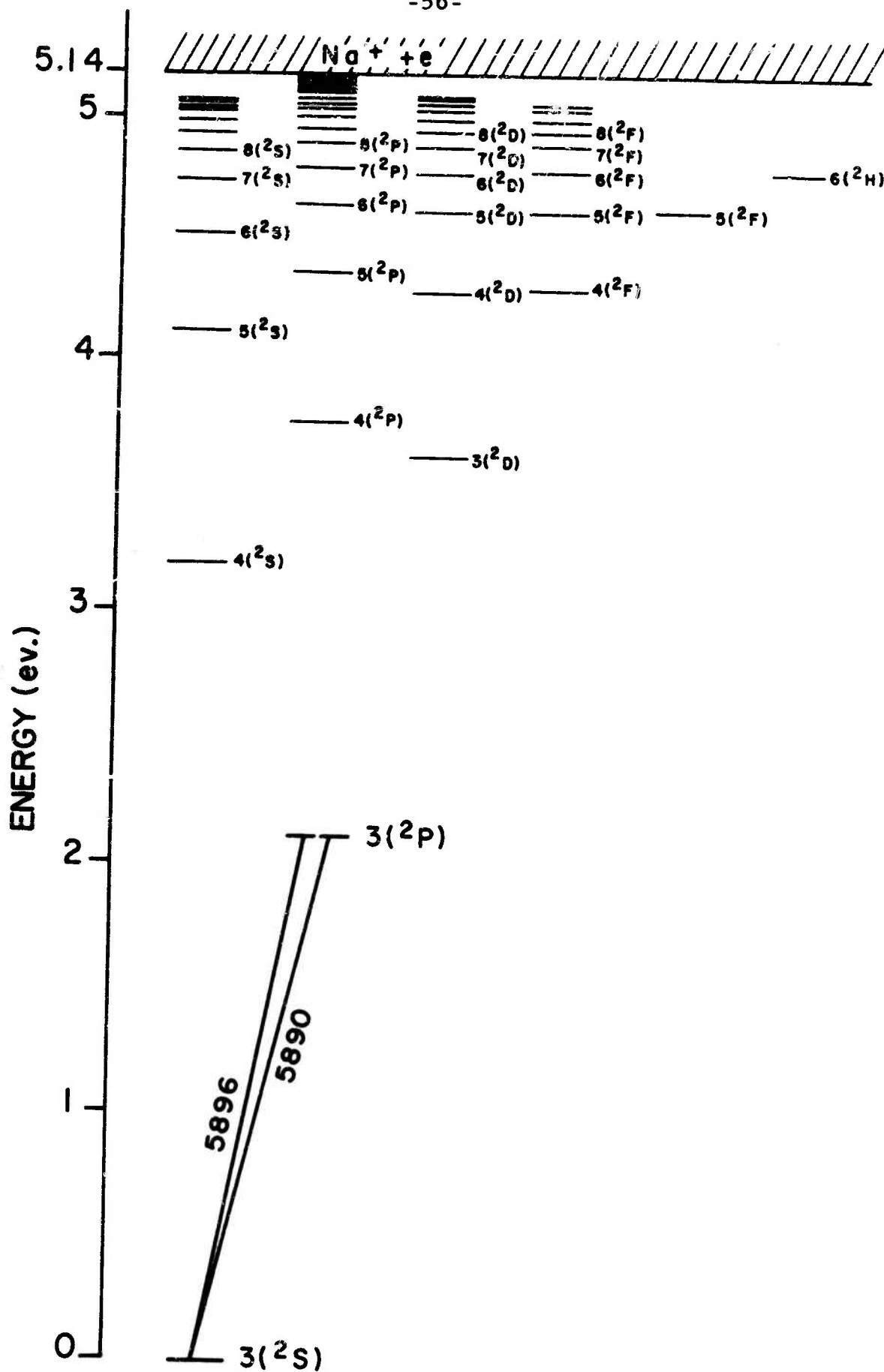


Figure 4. Sodium Energy Levels

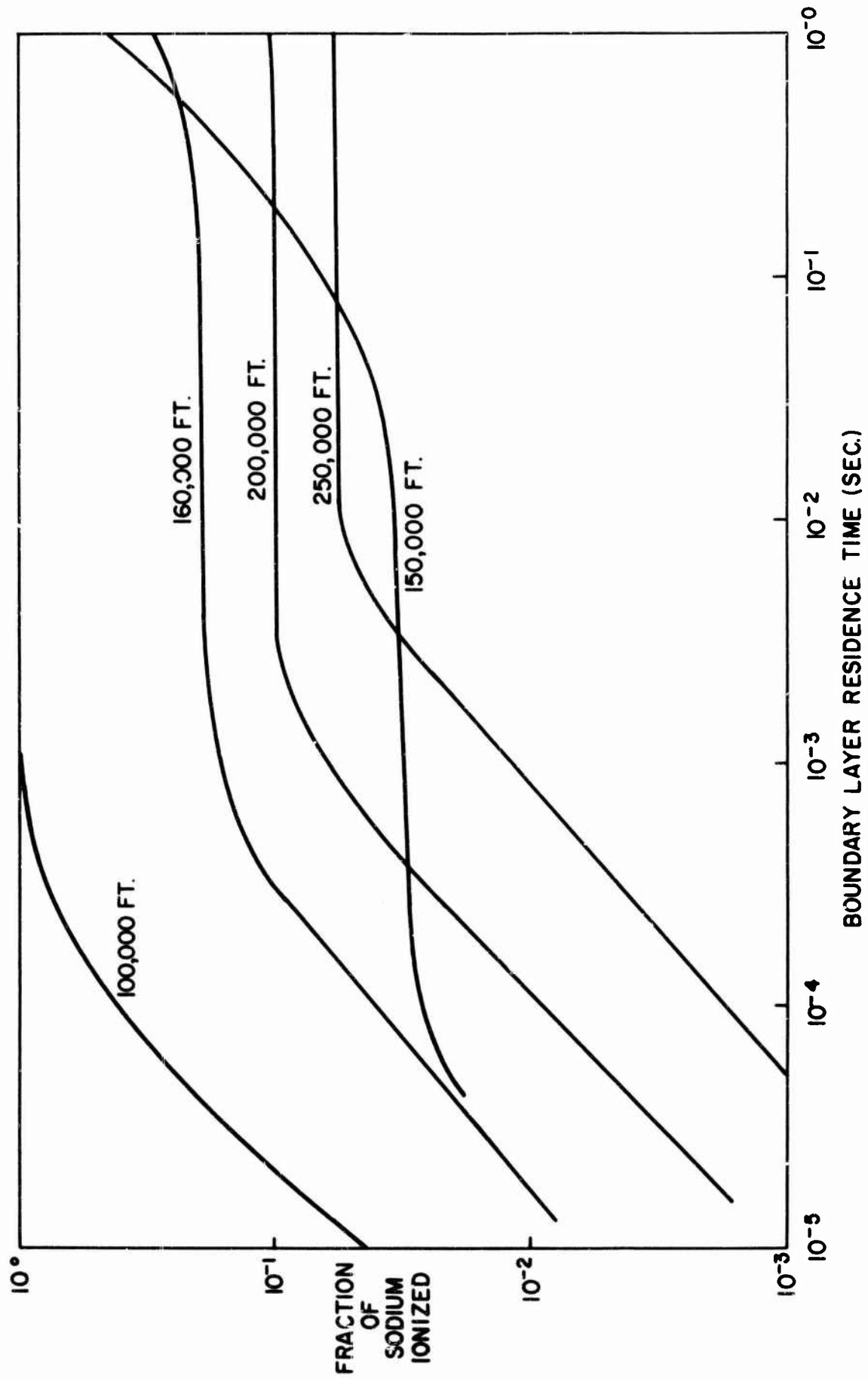


Figure 5. Rates of Sodium Ionization

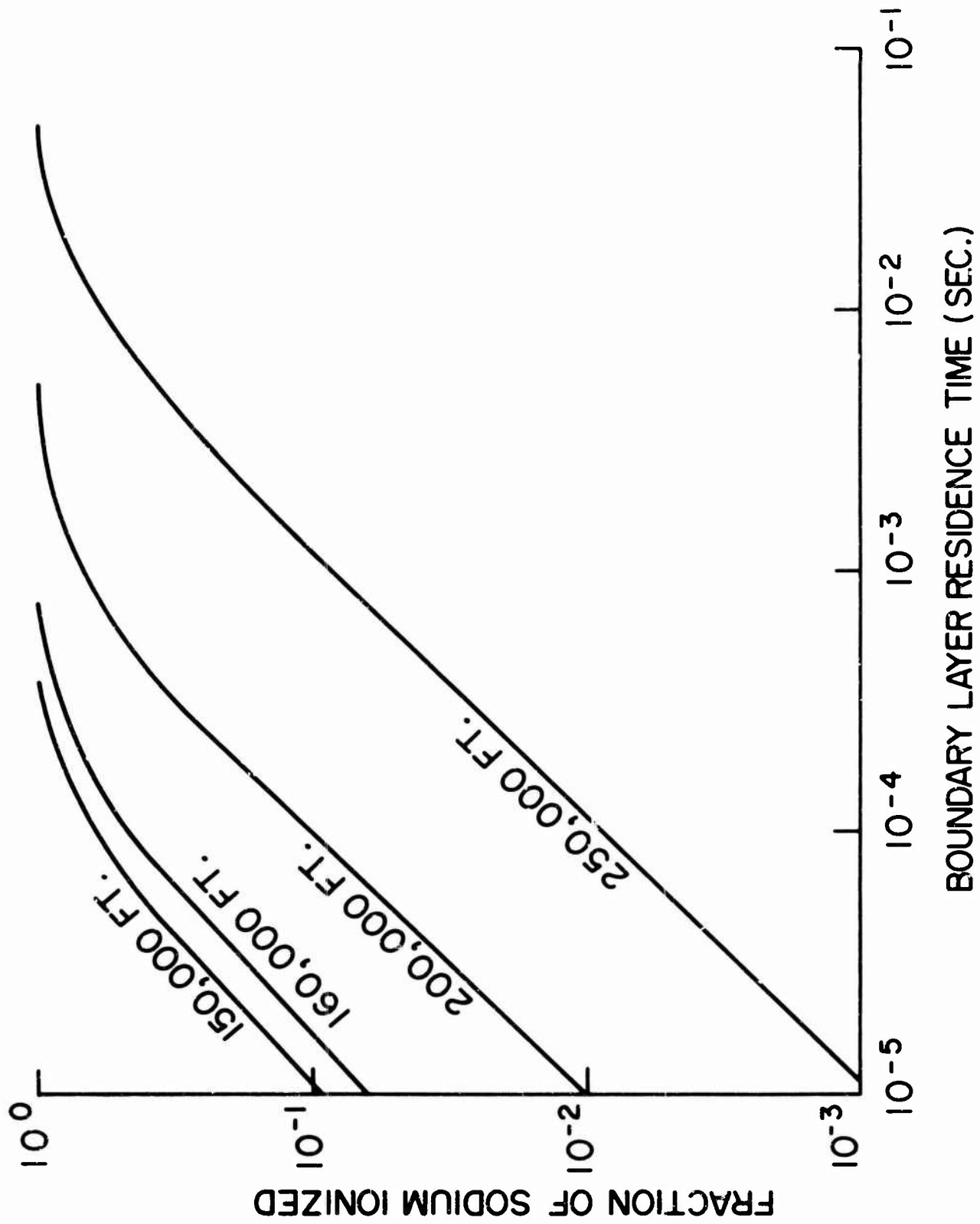


Figure 6. Rates of Sodium Ionization by Ion-Pair Formation

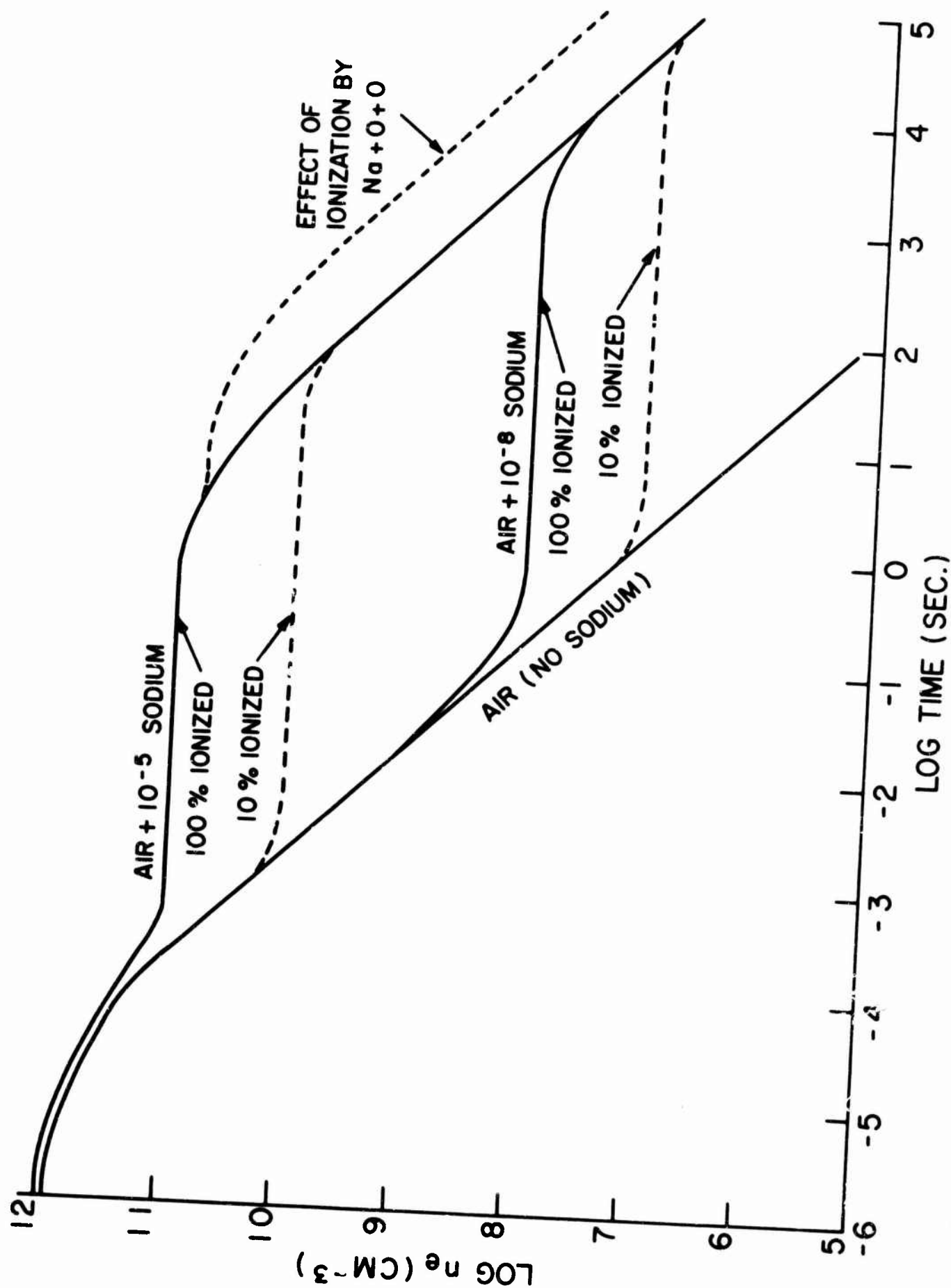


Figure 7. Effect of Sodium on Electron Density for Conditions Applicable to Wake at 200,000 Ft.

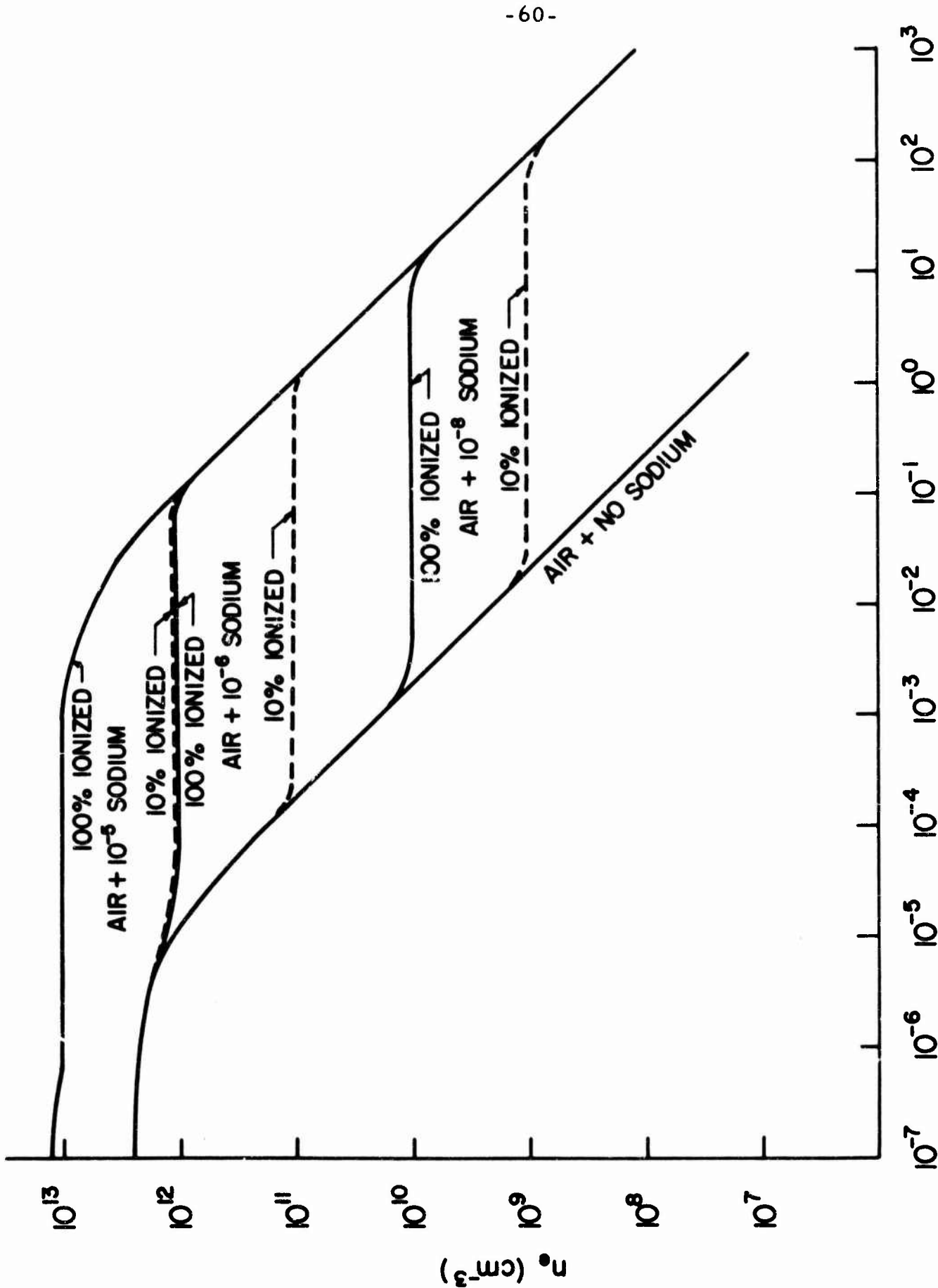


Figure 8. Effect of Sodium on Electron Density for Conditions Applicable to Wake at 50,000 Ft.

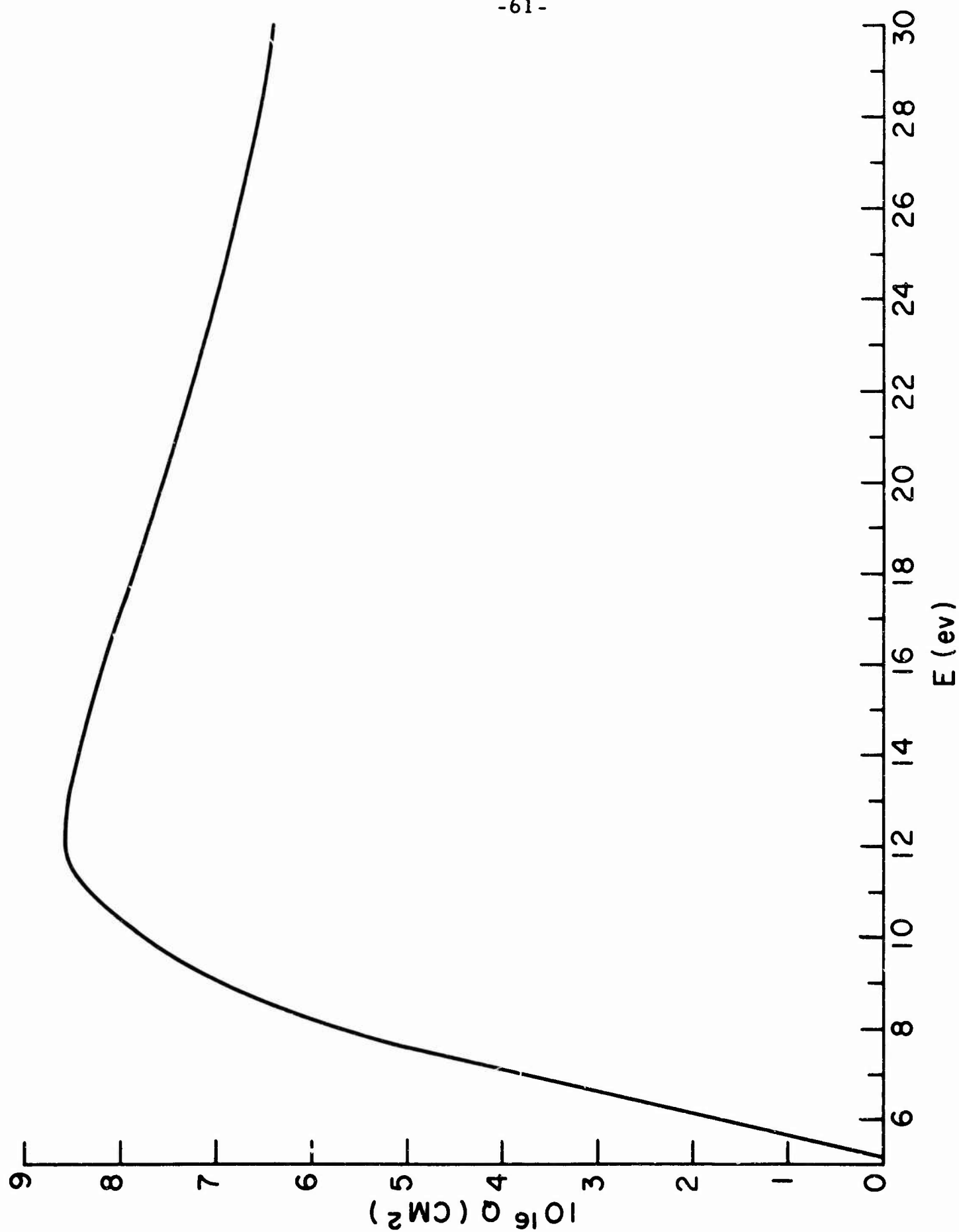


Figure 9. Cross-Section for Ionization of Sodium by Electron Collision (from Data of Tate and Smith)
Kaneko, and Brink)

TABLE I

Reactions of Sodium System

| | Ref. | ΔH | \underline{a} | \underline{b} | $\frac{10^3 c}{10^3 c}$ | $\frac{a^1}{10^3 c}$ | $\frac{b^1}{10^3 c}$ | $\frac{10^3 c^1}{10^3 c}$ |
|---|------|------------|-----------------|-----------------|-------------------------|----------------------|----------------------|---------------------------|
| Collisional excitation, Collisional deexcitation | | | | | | | | |
| 1. Na (3^2S) + M \rightleftharpoons Na (3^2P) + M | 9 | 2.11 | 6 (-10) | 0 | 24.7 | 2 (-10) | 0 | 0 |
| 2. Na (3^2S) + e \rightleftharpoons Na (3^2P) + e | 6 | 2.11 | 3 (-5) | 0 | 24.7 | 1 (-5) | 0 | 0 |
| 3. Na (3^2S) + M \rightleftharpoons Na (4^2P) + M | | 3.75 | 4 (-11) | 0 | 43.5 | 1 (-11) | 0 | 0 |
| 4. Na (3^2S) + e \rightleftharpoons Na (4^2P) + e | | 3.75 | 2 (-6) | 0 | 43.5 | 5 (-7) | 0 | 0 |
| 5. Na (3^2P) + M \rightleftharpoons Na (4^2S) + M | | 1.09 | 1 (-12) | 0 | 12.6 | 4 (-12) | 0 | 0 |
| 6. Na (3^2P) + e \rightleftharpoons Na (4^2S) + e | | 1.09 | 5 (-8) | 0 | 12.6 | 2 (-7) | 0 | 0 |
| 7. Na (4^2S) + M \rightleftharpoons Na (4^2P) + M | | 0.56 | 3 (-11) | 0 | 6.5 | 3 (-11) | 0 | 0 |
| 8. Na (4^2S) + e \rightleftharpoons Na (4^2P) + e | | 0.56 | 1.5 (-6) | 0 | 6.5 | 1.5 (-6) | 0 | 0 |
| Photoexcitation, Radiative deexcitation | | | | | | | | |
| 9. Na (3^2S) + $h\nu$ \leftarrow Na (3^2P) | 31 | | | | | 6.25 (7) | 0 | 0 |
| 10. Na (3^2S) + $h\nu$ \leftarrow Na (4^2P) | 31 | | | | | 2.85 (6) | 0 | 0 |
| 11. Na (3^2P) + $h\nu$ \leftarrow Na (4^2S) | 31 | | | | | 2.50 (7) | 0 | 0 |
| 12. Na (4^2S) + $h\nu$ \leftarrow Na (4^2P) | | | | | | 1.00 (7) | 0 | 0 |

$10^3 c^1$

b^1

a^1

$10^3 c$

b

a

ΔH

Ref.

Collisional ionization, Collisional deionization (3-body recombination)

| | | | | | | | | | | | | |
|-----|---------------------|---------------|--------------------------------------|------|------|-------|-----|------|---|-------|----|---|
| 13. | Na (3^2S) + M | \rightarrow | Na ⁺ + e + M | 5.14 | 1 | (-19) | 1.5 | 59.7 | 1 | (-35) | 0 | 0 |
| 14. | Na (3^2S) + e | \rightarrow | Na ⁺ + e + e | 5.14 | 4.33 | (-11) | 0.5 | 59.7 | 5 | (-27) | -1 | 0 |
| 15. | Na (3^2P) + M | \rightarrow | Na ⁺ + e + M | 3.03 | 1 | (-19) | 1.5 | 35.2 | 1 | (-35) | 0 | 0 |
| 16. | Na (3^2P) + e | \rightarrow | Na ⁺ + e + e | 3.03 | 4 | (-11) | 0.5 | 35.2 | 5 | (-27) | -1 | 0 |
| 17. | Na (4^2S) + M | \rightarrow | Na ⁺ + e + M | 1.95 | 1 | (-19) | 1.5 | 22.6 | 1 | (-35) | 0 | 0 |
| 18. | Na (4^2S) + e | \rightarrow | Na ⁺ + e + e | 1.95 | 4 | (-11) | 0.5 | 22.6 | 5 | (-27) | -1 | 0 |
| 19. | Na (4^2P) + M | \rightarrow | Na ⁺ + e + M | 1.39 | 1 | (-19) | 1.5 | 16.1 | 1 | (-35) | 0 | 0 |
| 20. | Na (4^2P) + e | \rightarrow | Na ⁺ + e + e | 1.39 | 4 | (-11) | 0.5 | 16.1 | 5 | (-27) | -1 | 0 |
| 21. | Na ₂ + M | \rightarrow | Na ₂ ⁺ + e + M | 5.2 | 1 | (-14) | 0 | 60 | 1 | (-28) | 0 | 0 |

Photoionization, Radiative deionization (radiative recombination)

| | | | | | | | | | | | | |
|-----|-------------------------|--------------|---------------------|-------|--|--|--|--|-----|-------|---|---|
| 22. | Na (3^2S) + h ν | \leftarrow | Na ⁺ + e | 32,20 | | | | | 1 | (-14) | 0 | 0 |
| 23. | Na (3^2P) + h ν | \leftarrow | Na ⁺ + e | | | | | | 1.6 | (-13) | 0 | 0 |
| 24. | Na (4^2S) + h ν | \leftarrow | Na ⁺ + e | | | | | | 1.8 | (-13) | 0 | 0 |
| 25. | Na (4^2P) + h ν | \leftarrow | Na ⁺ + e | | | | | | 2.4 | (-14) | 0 | 0 |

| Ref. | ΔH | a | b | $10^3 c$ | a^1 | b^1 | $10^3 c^1$ | | | |
|--|--|--------|-----|----------|-------|-------|------------|-------|-------|------|
| Association ionization, Dissociation deionization | | | | | | | | | | |
| 26. | $Na + O + O \rightleftharpoons Na^+ + e + O_2$ | 0.02 | 1 | (-32) | 0 | 0.232 | 1 | (-30) | 0 | 0 |
| 27. | $Na + N + N \rightleftharpoons Na^+ + e + N_2$ | - 4.62 | 1 | (-32) | 0 | 0 | 1 | (-30) | 0 | 53.5 |
| 28. | $Na + N + O \rightleftharpoons Na^+ + e + NO$ | - 1.35 | 1 | (-32) | 0 | 0 | 1 | (-30) | 0 | 15.6 |
| 29. | $Na + H + OH \rightleftharpoons Na^+ + e + H_2O$ | - 0.04 | 1 | (-32) | 0 | 0 | | | | |
| Associative ionization, Dissociative deionization (dissociative recombination) | | | | | | | | | | |
| 30. | $Na + H_2O \rightleftharpoons (Na \cdot H_2O)^+ + e$ | 3.0 | 1 | (-10) | 0 | 34.5 | 1 | (-8) | 0 | 0 |
| 31. | $Na + Na \rightleftharpoons Na_2^+ + e$ | 4.42 | 1 | (-12) | 0 | 51 | 1 | (-8) | 0 | 0 |
| 32. | $N + O \rightleftharpoons NO^+ + e$ | 2.76 | 1 | | | | | | | |
| Ion-pair formation, Ion-ion recombination (mutual neutralization) | | | | | | | | | | |
| 33. | $Na + O \rightleftharpoons Na^+ + O^-$ | 3.68 | 3.3 | (-9) | 0 | 43 | 2 | (-7) | - 0.5 | 0 |
| 34. | $Na + O_2 \rightleftharpoons Na^+ + O_2^-$ | 4.70 | 3 | (-9) | 0 | 54.5 | 2 | (-7) | - 0.5 | 0 |
| 35. | $Na + OH \rightleftharpoons Na^+ + OH^-$ | 3.36 | 3 | (-9) | 0 | 35 | 1 | (-7) | - 0.5 | 0 |
| 36. | $Na + NO_2 \rightleftharpoons Na^+ + NO_2^-$ | 2.1 | 3 | (-9) | 0 | 24.4 | 1 | (-7) | - 0.5 | 0 |
| 37. | $Na + Cl \rightleftharpoons Na^+ + Cl^-$ | 1.3 | | | | | 1 | (-7) | - 0.5 | 0 |
| 38. | $Na + F \rightleftharpoons Na^+ + F^-$ | 1.3 | | | | | 1 | (-7) | - 0.5 | 0 |

Ref. ΔH a b $10^3 c$ $\frac{a^1}{b^1}$ $\frac{10^3 c^1}{10^3 c}$

Ion-pair formation, Ion-ion recombination (mutual neutralization) - continued

| | | | | | | | | |
|-----|---|-----|--|--|---|-------|--|--|
| 39. | $NaO + M \rightleftharpoons Na^+ + O^- + M$ | 7.3 | | | 1 | (-29) | | |
| 40. | $NaO_2 + M \rightleftharpoons Na^+ + O_2^- + M$ | 6.4 | | | 1 | (-29) | | |
| 41. | $NaOH + M \rightleftharpoons Na^+ + OH^- + M$ | 7.4 | | | 1 | (-29) | | |
| 42. | $NaNO_2 + M \rightleftharpoons Na^+ + NO_2^- + M$ | 4.0 | | | 1 | (-29) | | |
| 43. | $NaCl + M \rightleftharpoons Na^+ + Cl^- + M$ | 4.9 | | | 1 | (-29) | | |
| 44. | $NaF + M \rightleftharpoons Na^+ + F^- + M$ | 6.6 | | | 1 | (-29) | | |

Collisional detachment, Collisional attachment

| | | | | | | | | | | | |
|-----|--|---|------|---|-------|---|------|---|-------|-------|---|
| 45. | $O^- + M \rightleftharpoons O + e + M$ | 2 | 1.46 | 1 | (-11) | 1 | 17.0 | 1 | (-27) | - 0.5 | 0 |
| 46. | $O_2^- + M \rightleftharpoons O_2 + e + M$ | 2 | 0.44 | 5 | (-13) | 1 | 5.1 | 1 | (-28) | - 0.5 | 0 |
| 47. | $OH^- + M \rightleftharpoons OH + e + M$ | | 1.78 | 1 | (-12) | 0 | 24.5 | 1 | (-28) | - 0.5 | 0 |
| 48. | $NO_2^- + M \rightleftharpoons NO_2 + e + M$ | | 3 | 1 | (-12) | 0 | 35 | 1 | (-28) | - 0.5 | 0 |
| 49. | $Cl^- + M \rightleftharpoons Cl + e + M$ | | 3.8 | 1 | (-11) | 0 | 44 | 1 | (-27) | - 0.5 | 0 |
| 50. | $F^- + M \rightleftharpoons F + e + M$ | | 3.8 | 1 | (-11) | 0 | 44 | 1 | (-27) | - 0.5 | 0 |
| 51. | $Na^- + M \rightleftharpoons Na + e + M$ | | 0.5 | 1 | (-11) | 0 | 5.8 | 1 | (-27) | - 0.5 | 0 |

| | Ref. | ΔH | \underline{a} | \underline{b} | $\underline{10^3 c}$ | $\underline{a^1}$ | $\underline{b^1}$ | $\underline{10^3 c^1}$ |
|---|------|------------|-----------------|-----------------|----------------------|-------------------|-------------------|------------------------|
| Photodetachment, Radiative attachment | | | | | | | | |
| 52. $O^- + h\nu \leftarrow O + e$ | 2 | | | | | 1.2 (-15) | 0 | 0 |
| 53. $O_2^- + h\nu \leftarrow O_2 + e$ | 2 | | | | | 1 (-18) | 0 | 0 |
| 54. $OH^- + h\nu \leftarrow OH + e$ | | | | | | 1 (-15) | 0 | 0 |
| 55. $NO_2^- + h\nu \leftarrow NO_2 + e$ | | | | | | 1 (-15) | 0 | 0 |
| 56. $Cl^- + h\nu \leftarrow Cl + e$ | | | | | | 1 (-15) | 0 | 0 |
| 57. $F^- + h\nu \leftarrow F + e$ | | | | | | 1 (-15) | 0 | 0 |
| 58. $Na^- + h\nu \leftarrow Na + e$ | | | | | | 1 (-15) | 0 | 0 |

-66-

Charge Transfer

| | | | | | | | | | |
|--|--------|---|-------|-------|---|---|-------|-------|----|
| 59. $Na + NO^+ \rightleftharpoons Na^+ + NO$ | - 4.11 | 5 | (-11) | - 0.5 | 0 | 5 | (-13) | - 0.5 | 45 |
| 60. $Na + N_2^+ \rightleftharpoons Na^+ + N_2$ | -10.44 | 5 | (-11) | - 0.5 | 0 | | | | |
| 61. $Na + O_2^+ \rightleftharpoons Na^+ + O_2$ | - 6.94 | 5 | (-11) | - 0.5 | 0 | | | | |
| 62. $Na + N^+ \rightleftharpoons Na^+ + N$ | - 9.40 | 5 | (-11) | - 0.5 | 0 | | | | |
| 63. $Na + O^+ \rightleftharpoons Na^+ + O$ | - 8.47 | 5 | (-11) | - 0.5 | 0 | | | | |
| 64. $Na + CHO^+ \rightleftharpoons Na^+ + CHO$ | < 0 | 5 | (-11) | - 0.5 | 0 | | | | |
| 65. $Na + H_3O^+ \rightleftharpoons Na^+ + H + H_2O$ | + 3.5 | 5 | (-11) | - 0.5 | 0 | | | | |

| Ref. | ΔH | a | b | $10^3 c$ | $\frac{1}{a}$ | $\frac{1}{b}$ | $\frac{10^3 c}{10^3 c}$ |
|--|------------|------|---|----------|---------------|---------------|-------------------------|
| Ion dissociation, Ion-neutral association | | | | | | | |
| 66. $(Na \cdot H_2O)^+ + M \rightleftharpoons Na^+ + H_2O + M$ | 33 | 2.2 | 1 | (-9) | 0 | 25.2 | 0 |
| 67. $Na_2^+ + M \rightleftharpoons Na^+ + Na + M$ | | 0.7 | 1 | (-9) | 0 | 8.1 | 0 |
| 68. $Na_2^+ + h\nu \leftarrow Na^+ + Na$ | | | | | 1 | (-15) | -0.5 |
| Dissociation, Recombination (compound formation) | | | | | | | |
| 69. $NaO + M \rightleftharpoons Na + O + M$ | 34 | 3.6 | 1 | (-9) | 0 | 40 | 0 |
| 70. $NaO_2 + M \rightleftharpoons Na + O_2 + M$ | 28 | 1.7 | 1 | (-9) | 0 | 20 | 0 |
| 71. $NaO_2 + M \rightleftharpoons NaO + O + M$ | | 3.2 | 1 | (-9) | 0 | 38 | 0 |
| 72. $Na_2O + M \rightleftharpoons Na + NaO + M$ | | 2.5 | 1 | (-9) | 0 | 30 | 0 |
| 73. $Na_2O + M \rightleftharpoons Na_2 + O + M$ | | 6.1 | 1 | (-9) | 0 | 71 | 0 |
| 74. $NaH + M \rightleftharpoons Na + H + M$ | | 2.05 | 1 | (-9) | 0 | 24 | 0 |
| 75. $NaOH + M \rightleftharpoons Na + OH + M$ | | 4.03 | 1 | (-9) | 0 | 47 | 0 |
| 76. $NaOH + M \rightleftharpoons NaO + H + M$ | | 4.7 | 1 | (-9) | 0 | 55 | 0 |
| 77. $Na_2 + M \rightleftharpoons Na + Na + M$ | | 0.76 | 1 | (-9) | 0 | 8.8 | 0 |
| 78. $O_2 + M \rightleftharpoons O + O + M$ | 1 | 5.12 | 2 | (-5) | -1 | 59.4 | 0 |
| 79. $N_2 + M \rightleftharpoons N + N + M$ | 1 | 9.76 | | | | | 0 |
| 80. $NO + M \rightleftharpoons N + O + M$ | 1 | 6.49 | | | | | 0 |

Ref. ΔH a b $10^3 c$ a^1 b^1 $10^3 c^1$
 Photodissociation, Radiative recombination (radiative compound formation)

| | | | | | | | | | | | |
|---------------|--|----|------|---|-------|---|-------|-------|-------|---|-----|
| 81. | $\text{NaO} + h\nu \leftarrow \text{Na} + \text{O}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 82. | $\text{NaO}_2 + h\nu \leftarrow \text{Na} + \text{O}_2$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 83. | $\text{NaO}_2 + h\nu \leftarrow \text{NaO} + \text{O}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 84. | $\text{Na}_2\text{O} + h\nu \leftarrow \text{Na}_2 + \text{O}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 85. | $\text{NaH} + h\nu \leftarrow \text{Na} + \text{H}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 86. | $\text{NaOH} + h\nu \leftarrow \text{Na} + \text{OH}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 87. | $\text{NaOH} + h\nu \leftarrow \text{NaO} + \text{H}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| 88. | $\text{Na}_2 + h\nu \leftarrow \text{Na} + \text{Na}$ | | | | | 1 | (-16) | - 0.5 | 0 | | |
| Rearrangement | | | | | | | | | | | |
| 89. | $\text{Na} + \text{O}_2 \rightleftharpoons \text{NaO} + \text{O}$ | 35 | 1.5 | 1 | (-13) | 0 | 17.5 | 1 | (-11) | 0 | 2 |
| 90. | $\text{Na} + \text{OH} \rightleftharpoons \text{NaO} + \text{H}$ | | 0.7 | 1 | (-11) | 0 | 10 | 1 | (-11) | 0 | 2.5 |
| 91. | $\text{Na} + \text{OH} \rightleftharpoons \text{NaH} + \text{O}$ | 34 | 2.2 | 1 | (-11) | 0 | 26 | 1 | (-11) | 0 | 1.4 |
| 92. | $\text{Na} + \text{H}_2 \rightleftharpoons \text{NaH} + \text{H}$ | | 2.43 | 1 | (-11) | 0 | 28 | 1 | (-11) | 0 | 1.4 |
| 93. | $\text{Na} + \text{H}_2\text{O} \rightleftharpoons \text{NaH} + \text{OH}$ | | 3.13 | 1 | (-12) | 0 | 37 | 1 | (-11) | 0 | 1.4 |
| 94. | $\text{Na} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{H}$ | | 1.15 | 1 | (-12) | 0 | 13.5 | 1 | (-12) | 0 | 2.8 |
| 95. | $\text{Na} + \text{NO} \rightleftharpoons \text{NaO} + \text{N}$ | | 2.9 | 1 | (-11) | 0 | 34 | 1 | (-11) | 0 | 2 |

Rearrangement - continued

| Rearrangement - continued | | | | | | | | | | | | |
|---------------------------|-----------|--------------------------------|-----------------|-----------------|--------------------------------|---------------------------|---------------------------|--------------------------------|--------------------|-------|---|-----|
| | Ref. | ΔH | \underline{a} | \underline{b} | $\frac{10^3 c}{\underline{a}}$ | $\frac{1}{\underline{a}}$ | $\frac{1}{\underline{b}}$ | $\frac{10^3 c}{\underline{b}}$ | $\frac{1}{10^3 c}$ | | | |
| 96. | NaO + O2 | \rightleftharpoons NaO2 + O | 36 | 1.9 | 1 | (-12) | 0 | 22 | 1 | (-11) | 0 | 2 |
| 97. | NaO + O2 | \rightleftharpoons Na + O3 | 34 | 0.6 | 1 | (-12) | 0 | 31 | 1 | (-11) | 0 | 0 |
| 98. | NaO + N2 | \rightleftharpoons Na + N2O | | 1.32 | 1 | (-12) | 0 | 16 | 1 | (-12) | 0 | 1 |
| 99. | NaO + NO | \rightleftharpoons Na + NO2 | | 0.4 | 1 | (-12) | 0 | 7.1 | 1 | (-12) | 0 | 2 |
| 100. | NaO + NO | \rightleftharpoons NaO2 + N | | 3.3 | 1 | (-12) | 0 | 4.8 | 1 | (-12) | 0 | 1 |
| 101. | NaO + H | \rightleftharpoons NaH + O | | 1.5 | 1 | (-11) | 0 | 19 | 1 | (-11) | 0 | 1.4 |
| 102. | NaO + OH | \rightleftharpoons NaO2 + H | | 1.1 | 1 | (-12) | 0 | 15 | 1 | (-12) | 0 | 2.2 |
| 103. | NaO + OH | \rightleftharpoons NaOH + O2 | | 0.7 | 1 | (-12) | 0 | 31 | 1 | (-12) | 0 | 23 |
| 104. | NaO + Na | \rightleftharpoons Na2 + O | | 2.8 | 1 | (-11) | 0 | 35 | 1 | (-11) | 0 | 0.5 |
| 105. | NaO2 + Na | \rightleftharpoons Na2 + O2 | | 0.9 | 1 | (-12) | 0 | 11 | 1 | (-12) | 0 | 0.5 |
| 106. | NaO2 + O2 | \rightleftharpoons NaO + O3 | | 0.6 | 1 | (-12) | 0 | 27 | 1 | (-12) | 0 | 0.6 |
| 107. | NaO2 + O | \rightleftharpoons Na + O3 | | 2.1 | 1 | (-12) | 0 | 8 | 1 | (-12) | 0 | 1 |
| 108. | NaOH + O | \rightleftharpoons NaO2 + H | | 1.5 | 1 | (-12) | 0 | 20 | 1 | (-12) | 0 | 2.2 |
| 109. | NaOH + O | \rightleftharpoons NaO + OH | | 0.4 | 1 | (-12) | 0 | 7.7 | 1 | (-12) | 0 | 3 |
| 110. | NaOH + O2 | \rightleftharpoons NaO2 + OH | | 2.3 | 1 | (-13) | 0 | 28 | | | | |
| 111. | NaOH + H | \rightleftharpoons NaO + H2 | | 0.2 | 1 | (-12) | 0 | 5.5 | 1 | (-12) | 0 | 3.1 |

| | | Ref. | ΔH | a | b | $10^3 c$ | $\frac{a^1}{a}$ | $\frac{b^1}{b}$ | $\frac{10^3 c^1}{10^3 c}$ |
|---|---|-----------|------------|-------|---|----------|-----------------|-----------------|---------------------------|
| Chemical-excitation, Chemi-deexcitation | | | | | | | | | |
| 112. | $Na (3^2S) + O + O \rightleftharpoons Na (3^2P) + O_2$ | - 3.01 | 1^{-32} | 0 | 0 | 1 | (-11) | 0 | 35.0 |
| 113. | $Na (3^2S) + N + O \rightleftharpoons Na (3^2P) + NO$ | - 4.38 | 1 | (-32) | 0 | 1 | (-11) | 0 | 50.8 |
| 114. | $Na (3^2S) + N + N \rightleftharpoons Na (3^2P) + N_2$ | - 7.65 | 1 | (-32) | 0 | 1 | (-11) | 0 | 88.8 |
| 115. | $Na (3^2S) + H + H \rightleftharpoons Na (3^2P) + H_2$ | 37 - 2.37 | 1 | (-32) | 0 | 1 | (-11) | 0 | 27.5 |
| 116. | $Na (3^2S) + H + O \rightleftharpoons Na (3^2P) + OH$ | - 2.20 | 1 | (-32) | 0 | 1 | (-11) | 0 | 25.6 |
| 117. | $Na (3^2S) + O + O_2 \rightleftharpoons Na (3^2P) + O_3$ | + 1.05 | 1 | (-32) | 0 | 13.0 | 1 | (-11) | 0.8 |
| 118. | $Na (3^2S) + N_2 + O \rightleftharpoons Na (3^2P) + N_2O$ | + 0.41 | 1 | (-32) | 0 | 6.0 | 1 | (-11) | 1.2 |
| 119. | $Na (3^2S) + H + OH \rightleftharpoons Na (3^2P) + H_2O$ | 37 - 3.08 | 1 | (-32) | 0 | 0 | 1 | (-11) | 35.8 |
| 120. | $Na (3^2S) + NO^+ + e \rightleftharpoons Na (3^2P) + N + O$ | - 0.64 | 1 | (-32) | 0 | 0 | 1 | (-32) | 7.4 |
| 121. | $Na (3^2S) + NO^+ + e \rightleftharpoons Na (3^2P) + NO$ | - 7.15 | 1 | (-29) | 0 | 0 | 1 | (-11) | 83 |

TABLE II

Conditions for Calculations of Instantaneous Rates

| | <u>Altitude</u> (10^3 ft) | <u>T</u> (°K) | <u>n</u> (cm^{-3}) | <u>Notes</u> |
|---|---------------------------------|------------------|----------------------------------|--|
| A | 200 | 5000 | 3.27 (16) | 50% ionization of sodium |
| B | 150 | 5000 | 2.12 (15) | 50% ionization; high NaX cone; high H ₂ O dissociation |
| C | 150 | 5000 | 2.12 (15) | 50% ionization; high H ₂ O dissociation |
| D | 150 | 5000 | 3.16 (15) | * |
| E | 150 | 4000 | 3.22 (15) | * |
| F | 150 | 3000 | 4.14 (15) | * |
| G | 150 | 2000 | 5.30 (15) | * |
| H | 150 | 1000 | 1.06 (16) | * |
| I | 150 | 1000 | 1.06 (16) | Distribution among Na states is that of 5000°K equilibrium. |
| J | 100 | 5000 | 1.60 (16) | 10^{-5} Na; 10% ionization |
| K | 100 | 5000 | 1.60 (16) | 10^{-7} Na; 10% ionization |
| L | 60 | 5000 | 1.10 (17) | 90% ionization |

* Used 50% ionization at start of wake (D) with slight decrease downstream (E, F, G, H).

TABLE II (Continued)

Concentrations

| | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> | <u>E</u> | <u>F</u> | <u>G</u> | <u>H</u> | <u>I</u> | <u>J</u> | <u>K</u> | <u>L</u> |
|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| h (10^3 ft) | 200 | 150 | 150 | 150 | 150 | 150 | 150 | 150 | 150 | 100 | 100 | 60 |
| T ($^{\circ}K$) | 5000 | 5000 | 5000 | 5000 | 4000 | 3000 | 2000 | 1000 | 1000 | 5000 | 5000 | 5000 |
| n (cm^{-3}) | | | | | | | | | | | | |
| M | 3.27(14) | 2.12(15) | 2.12(15) | 3.16(15) | 3.22(15) | 4.14(15) | 5.30(15) | 1.06(16) | 1.06(16) | 1.60(16) | 1.60(16) | 1.10(17) |
| Na | 1.00(9) | 1.00(10) | 1.00(10) | 1.00(10) | 1.25(10) | 1.67(10) | 2.50(10) | 5.00(10) | 1.00(10) | 1.00(11) | 1.00(9) | 1.00(11) |
| Na (3S) | 9.92(8) | 9.92(9) | 9.92(9) | 9.92(9) | 1.25(10) | 1.67(10) | 2.50(10) | 5.00(10) | 9.92(9) | 9.92(10) | 9.92(8) | 9.92(10) |
| Na (3P) | 2.06(7) | 2.06(8) | 2.06(8) | 2.06(8) | 7.44(7) | 1.24(7) | 2.92(5) | 2.28(0) | 2.06(8) | 2.06(9) | 2.06(7) | 2.06(9) |
| Na (4S) | 5.62(5) | 5.62(6) | 5.62(6) | 5.62(6) | 1.06(6) | 6.21(4) | 1.81(2) | 2.67(-6) | 5.62(6) | 5.62(7) | 5.62(5) | 5.62(7) |
| Na (4P) | 4.95(5) | 4.95(6) | 4.95(6) | 4.95(6) | 6.90(5) | 2.52(4) | 2.68(0) | 1.92(-8) | 4.95(6) | 4.95(7) | 4.95(5) | 4.95(7) |
| e | 7.45(10) | 3.44(11) | 3.44(11) | 3.44(11) | 5.00(10) | 1.60(10) | 1.20(10) | 1.00(10) | 1.00(7) | 3.00(10) | 2.00(10) | 9.00(12) |
| Na^+ | 1.00(9) | 1.00(10) | 1.00(10) | 4.00(10) | 2.00(10) | 1.50(10) | 1.20(10) | 1 | (10) | 1.00(7) | 1.00(10) | 1.00(8) |
| Na_2^+ | 1.00(-3) | 1.00(6) | 1.00(6) | 1 | (3) | 1 | (2) | 1 | (0) | 1 | (-1) | 1.00(4) |
| Na^- | 1.00(3) | 1.00(3) | 1.6 | (4) | 1.6 | (4) | 4.3 | (3) | 3.4 | (3) | 1.24(4) | 5.2 |
| | | | | | | | | | | | | |

| | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> | <u>E</u> | <u>F</u> | <u>G</u> | <u>H</u> | <u>I</u> | <u>J</u> | <u>K</u> | <u>L</u> | | | | | | | | | | | | |
|-------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----|------|------|------|------|------|------|------|---|------|---|------|
| H | 1 | (12) | 1 | (13) | 1 | (13) | 3 | (12) | 1 | (12) | 3 | (11) | 1 | (11) | 1 | (13) | 1 | (13) | 1 | (14) | | | | |
| H ₂ | 1 | (6) | 1 | (6) | 1 | (9) | 3 | (9) | 1 | (10) | 3 | (10) | 1 | (11) | 1 | (10) | 1 | (9) | 1 | (11) | | | | |
| OH | 1 | (11) | 1 | (11) | 1 | (12) | 3 | (11) | 1 | (11) | 3 | (10) | 1 | (10) | 1 | (11) | 1 | (12) | 1 | (13) | | | | |
| H ₂ O | 1 | (9) | 1 | (4) | 1 | (10) | 3 | (10) | 1 | (11) | 3 | (11) | 1 | (12) | 1 | (10) | 1 | (11) | 1 | (13) | | | | |
| O | 7.70(13) | 5.95(14) | 5.95(14) | 8.9 | (14) | 1.09(15) | 1.35(15) | 5.3 | (13) | 6 | (7) | 1 | (8) | 5 | (15) | 5 | (15) | 3.6 | (16) | | | | | |
| O ₂ | 1.00(8) | 8.75(9) | 8.75(9) | 1.41(10) | 3.06(11) | 7.08(13) | 1.06(15) | 2.14(15) | 2 | (15) | 2 | (12) | 2 | (12) | 2 | (12) | 3 | (13) | | | | | | |
| N | 2.10(14) | 8.03(14) | 8.03(14) | 1.19(15) | 1.1 | (14) | 3.3 | (12) | 1 | (8) | 1 | (-4) | 1 | (2) | 3 | (15) | 3 | (15) | 1.5 | (16) | | | | |
| N ₂ | 3.80(13) | 7.09(14) | 7.09(14) | 1.08(15) | 2.01(15) | 2.72(15) | 4.13(15) | 8.28(15) | 8 | (15) | 6 | (15) | 6 | (15) | 6 | (15) | 6 | (15) | 6 | (16) | | | | |
| NO | 3 | (10) | 1.23(12) | 2 | (11) | 1.06(13) | 4.2 | (13) | 3.5 | (13) | 1 | (13) | 1 | (8) | 2 | (13) | 2 | (13) | 6 | (14) | | | | |
| Na ₂ | 1 | (-2) | 1 | (6) | 2 | (-1) | 1 | (0) | 1 | (1) | 1 | (2) | 1 | (3) | 1 | (4) | 1 | (-2) | 1 | (2) | 1 | (0) | 1 | (3) |
| NaO | 1 | (3) | 1 | (9) | 1 | (5) | 6.7 | (5) | 3.1 | (5) | 2.4 | (5) | 2.2 | (6) | 5.8 | (6) | 1 | (3) | 1 | (6) | 1 | (4) | 1 | (7) |
| NaO ₂ | 1 | (-2) | 1 | (7) | 5 | (0) | 7.5 | (0) | 4.2 | (2) | 4.0 | (5) | 4.0 | (8) | 1 | (10) | 1 | (-2) | 1 | (2) | 1 | (0) | 1 | (3) |
| NaH | 1 | (1) | 1 | (9) | 2 | (3) | 1.2 | (4) | 6.6 | (2) | 1.5 | (2) | 5.6 | (2) | 1.9 | (6) | 1 | (1) | 1 | (5) | 1 | (3) | 1 | (6) |
| NaOH | 1 | (1) | 1 | (9) | 1 | (3) | 1 | (3) | 3 | (3) | 1 | '4) | 3 | (4) | 1 | (5) | 1 | (1) | 1 | (4) | 1 | (2) | 1 | (5) |
| Na ₂ O | 1 | (-6) | 1 | (4) | 4 | (-4) | 1 | (-3) | 1 | (-2) | 1 | (-1) | 1 | (0) | 1 | (1) | 1 | (-6) | 1 | (-2) | 1 | (-4) | 1 | (-1) |

| | <u>A</u> | <u>B</u> | <u>C</u> | <u>D</u> | <u>E</u> | <u>F</u> | <u>G</u> | <u>H</u> | <u>I</u> | <u>J</u> | <u>K</u> | <u>L</u> | |
|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|--------|
| O^+ | 1 | (10) | 1.47(10) | 1.47(10) | 1.3 (11) | 7 (8) | 4.5 (3) | 2.7 (-6) | 1 (-32) | 1 (0) | 5 (8) | 5 (8) | 1 (11) |
| O_2^+ | 1 | (6) | 1.68(7) | 1.68(7) | 2.8 (7) | 3.8 (4) | 3.8 (3) | 4.2 (-2) | 4.3(-21) | 1 (2) | 2 (6) | 2 (6) | 3 (9) |
| N^+ | 2 | (10) | 1.12(10) | 1.12(10) | 1.5 (10) | 2.9 (6) | 3.3 (0) | 6 (-13) | 3 (-50) | 1 (0) | 2 (8) | 2 (8) | 2 (10) |
| N_2^+ | 3 | (8) | 1.06(9) | 1.06(9) | 1.6 (9) | 2.4 (6) | 4.6 (1) | 6.6 (-8) | 2.2(-35) | 1 (2) | 3 (7) | 3 (7) | 1 (10) |
| NO^+ | 4.3 (10) | 3.07(11) | 3.07(11) | 1.6 (11) | 3 (10) | 1 (9) | 1 (5) | 1 (-6) | 1 (4) | 1 (10) | 1 (10) | 7 (12) | |
| CHO^+ | 1 | (8) | 1 (10) | 1 (9) | 3 (8) | 1 (8) | 3 (7) | 1 (7) | 1 (0) | 1 (10) | 1 (10) | 1 (12) | |
| $(Na \cdot H_2O)^+$ | 4.8 (-1) | | 5.9 (-4) | | | | | | 2.9 (7) | 1.5 (4) | 1 (4) | 1.3 (5) | |
| O^- | 1 | (5) | 3.69(6) | 3.63(6) | 2.02(6) | 3.83(6) | 3.36(4) | 3.18(2) | 1 (5) | 5 (6) | 5 (6) | 5 (9) | |
| O_2^- | 1 | (-3) | 3 (2) | 1.91(6) | 5.10(1) | 7.62(3) | 3.67(5) | 2.24(7) | 1 (5) | 1 (4) | 1 (4) | 1 (6) | |
| OH^- | 1 | (2) | 1 (6) | 7.52(8) | 2.66(8) | 4.69(6) | 1.05(5) | 2.74(4) | 1 (3) | 1 (6) | 1 (6) | 1 (8) | |

TABLE III

Na⁺ Kinetics

| <u>Conditions</u> | <u>Reactions forming</u> | | <u>Reactions consuming</u> | |
|-------------------|---|----------|---|---------|
| A | Na + O → Na ⁺ + O ⁻ | 4.7 (10) | Na ⁺ + e → Na + hν | 2.8 (7) |
| | Na + NO ⁺ → Na ⁺ + NO | 3.2 (8) | | |
| | Na + OH → Na ⁺ + OH ⁻ | 2.7 (8) | Na ⁺ + O ⁻ → Na + O | 2.8 (5) |
| | Na + e → Na ⁺ + 2e | 5.4 (6) | | |
| B | Na + O → Na ⁺ + O ⁻ | 3.6 (12) | Na ⁺ + e → Na + hν | 1.3 (9) |
| | Na + OH → Na ⁺ + OH ⁻ | 2.7 (9) | Na ⁺ + O ⁻ → Na + C | 1.0 (8) |
| | Na + e → Na ⁺ + 2e | 5.0 (8) | Na ⁺ + OH ⁻ → Na + OH | 1.4 (1) |
| C | Na + O → Na ⁺ + O ⁻ | 3.6 (12) | Na ⁺ + e → Na + hν | 1.3 (9) |
| | Na + OH → Na ⁺ + OH ⁻ | 2.7 (9) | Na ⁺ + O ⁻ → Na + O | 1.0 (8) |
| | Na + e → Na ⁺ + 2e | 5.0 (8) | Na ⁺ + OH ⁻ → Na + OH | 1.4 (7) |

| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> |
|-------------------|---|---|
| D | $\text{Na} + \text{O} \longrightarrow \text{Na}^+ + \text{O}^-$ | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na} + \text{OH}$ 1.1 (10) |
| | $\text{Na} + \text{OH} \longrightarrow \text{Na}^+ + \text{OH}^-$ | $\text{Na}^+ + e \longrightarrow \text{Na} + h\nu$ 1.3 (9) |
| | $\text{Na} + \text{NO}^+ \longrightarrow \text{Na}^+ + \text{NO}$ | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na} + \text{O}$ 1.0 (8) |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow \text{Na}^+ + e + \text{O}_2$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na} + \text{O}_2$ 5.4 (7) |
| | | $\text{Na} + \text{OH}^- + \text{M} \longrightarrow \text{NaOH} + \text{M}$ 2.4 (5) |
| E | $\text{Na} + \text{O} \longrightarrow \text{Na}^+ + \text{O}^-$ | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na} + \text{OH}$ 5.0 (9) |
| | $\text{Na} + \text{OH} \longrightarrow \text{Na}^+ + \text{OH}^-$ | $\text{Na}^+ + e \longrightarrow \text{Na} + h\nu$ 3.5 (8) |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow \text{Na}^+ + e + \text{O}_2$ | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na} + \text{O}$ 7.7 (7) |
| | $\text{Na} + \text{N} + \text{O} \longrightarrow \text{Na}^+ + e + \text{NO}$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na} + \text{O}_2$ 1.9 (7) |
| | $\text{Na} + \text{O}_2 \longrightarrow \text{Na}^+ + \text{O}_2^-$ | $(\text{Na} \cdot \text{H}_2\text{O})^+ + e \longrightarrow \text{Na} + \text{H}_2\text{O}$ 5.2 (5) |
| | $(\text{Na} \cdot \text{H}_2\text{O})^+ + \text{M} \longrightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{M}$ | $\text{Na}^+ + 2e \longrightarrow \text{Na} + e$ 4.2 (5) |
| | | $\text{Na}^+ + \text{OH}^- + \text{M} \longrightarrow \text{NaOH} + \text{M}$ 1.0 (5) |
| | | |

| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> |
|-------------------|---|---|
| F | $\text{Na} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na} + \text{O} \quad 2.1 \text{ (8)}$ |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na} + \text{OH} \quad 1.3 \text{ (8)}$ |
| | $\text{Na} + \text{NO}^+ \longrightarrow$ | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + h\nu \quad 9.0 \text{ (7)}$ |
| | $\text{Na} + \text{O}_2 \longrightarrow$ | $\text{Na}^+ + 2\text{e} \longrightarrow \text{Na} + \text{e} \quad 2.8 \text{ (6)}$ |
| | $\text{Na} + \text{OH} \longrightarrow$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na} + \text{O}_2 \quad 4.2 \text{ (5)}$ |
| | $(\text{Na} \cdot \text{H}_2\text{O})^+ + \text{M} \longrightarrow$ | $\text{Na}^+ + \text{Na} + \text{M} \longrightarrow \text{Na}_2^+ + \text{M} \quad 1.0 \text{ (5)}$ |
| | | $\text{Na}^+ + \text{e} + \text{O}_2 \longrightarrow \text{Na} + \text{O} + \text{O} \quad 1.7 \text{ (4)}$ |
| | | $\text{Na}^+ + \text{Na} \longrightarrow \text{Na}_2^+ + h\nu \quad 4.6 \text{ (3)}$ |
| | | |
| | | |
| G | $\text{Na} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + h\nu \quad 5.4 \text{ (7)}$ |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na} + \text{O}_2 \quad 3.3 \text{ (7)}$ |
| | $\text{Na} + \text{O}_2 \longrightarrow$ | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na} + \text{OH} \quad 4.7 \text{ (6)}$ |
| | $\text{Na} + \text{OH} \longrightarrow$ | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na} + \text{O} \quad 3 \text{ (6)}$ |
| | $\text{Na}_2^+ + \text{M} \longrightarrow$ | $\text{Na}^+ + \text{Na} + \text{M} \longrightarrow \text{Na}_2^+ + \text{M} \quad 1.6 \text{ (5)}$ |
| | $\text{Na} + \text{CHO}^+ \longrightarrow$ | $\text{Na}^+ + 2\text{e} \longrightarrow \text{Na} + \text{e} \quad 9.2 \text{ (4)}$ |
| | $(\text{Na} \cdot \text{H}_2\text{O})^+ + \text{M} \longrightarrow$ | $\text{Na}^+ + \text{Na} \longrightarrow \text{Na}_2^+ + h\nu \quad 6.7 \text{ (3)}$ |
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| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> |
|-------------------|--|---|
| H | $\text{Na}_2^+ + \text{M} \longrightarrow \text{Na}^+ + \text{Na} + \text{M}$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na} + \text{O}_2$ 5.7 (9) |
| | $\text{Na} + \text{CHO}^+ \longrightarrow \text{Na}^+ + \text{CHO}$ | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + \text{h}\nu$ 1.5 (8) |
| | $\text{Na} + \text{H} + \text{OH} \longrightarrow \text{Na}^+ + \text{e} + \text{H}_2\text{O}$ | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na} + \text{OH}$ 3.4 (6) |
| | | $\text{Na}^+ + 2\text{e} \longrightarrow \text{Na} + \text{e}$ 3.2 (6) |
| | | $\text{Na}^+ + \text{Na} + \text{M} \longrightarrow \text{Na}_2^+ + \text{M}$ 2.1 (6) |
| | | $\text{Na}^+ + \text{O}_2^- + \text{M} \longrightarrow \text{NaO}_2 + \text{M}$ 9.5 (4) |
| | | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na} + \text{O}$ 8.0 (4) |
| | | $\text{Na}^+ + \text{Na} \longrightarrow \text{Na}_2^+ + \text{h}\nu$ 6.3 (4) |
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| | | |
| I | $\text{Na} + \text{NO}^+ \longrightarrow \text{Na}^+ + \text{NO}$ | $\text{Na}^+ + \text{C}_2^- \longrightarrow \text{Na} + \text{O}_2$ 6.3 (3) |
| | $\text{Na} (4^2\text{P}) + \text{e} \longrightarrow \text{Na}^+ + 2\text{e}$ | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na} + \text{O}$ 6.3 (3) |
| | $\text{Na} + \text{H} + \text{OH} \longrightarrow \text{Na}^+ + \text{e} + \text{H}_2\text{O}$ | $\text{Na}^+ + 2\text{e} \longrightarrow \text{Na} + \text{e}$ 1.9 (2) |
| | $\text{Na}_2^+ + \text{M} \longrightarrow \text{Na}^+ + \text{Na} + \text{M}$ | $\text{Na}^+ + \text{Na} + \text{M} \longrightarrow \text{Na}_2^+ + \text{M}$ 1.1 (2) |
| | $\text{Na} (4^2\text{P}) + \text{M} \longrightarrow \text{Na}^+ + \text{e} + \text{M}$ | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + \text{h}\nu$ 3.7 (1) |
| | | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na} + \text{OH}$ 3.2 (1) |
| | | $\text{Na}^+ + \text{Na} \longrightarrow \text{Na}_2^+ + \text{h}\nu$ 3.2 (0) |

| <u>Conditions</u> | <u>Reactions forming</u> | | <u>Reactions consuming</u> | |
|-------------------|---|--------------------------------|--|------------------------------------|
| J | $\text{Na} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{O}^-$ | $\text{Na}^+ + 2e \longrightarrow$ | $\text{Na} + e$ 3.2 (8) |
| | $\text{Na} + \text{OH} \longrightarrow$ | $\text{Na}^+ + \text{OH}^-$ | $\text{Na}^+ + \text{O}^- \longrightarrow$ | $\text{Na} + \text{O}$ 1.4 (8) |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow$ | $\text{Na}^+ + e + \text{O}_2$ | $\text{Na}^+ + e \longrightarrow$ | $\text{Na} + h\nu$ 1.1 (8) |
| | $\text{Na} + \text{N} + \text{O} \longrightarrow$ | $\text{Na}^+ + e + \text{NO}$ | $\text{Na}^+ + \text{OH}^- \longrightarrow$ | $\text{Na} + \text{OH}$ 1.4 (7) |
| | $\text{Na} + \text{O}_2 \longrightarrow$ | $\text{Na}^+ + \text{O}_2^-$ | $\text{Na}^+ + \text{Na} + \text{M} \longrightarrow$ | $\text{NO}_2^+ + \text{M}$ 1.6 (6) |
| | $\text{Na} + \text{N} + \text{N} \longrightarrow$ | $\text{Na}^+ + e + \text{N}_2$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow$ | $\text{Na} + \text{O}_2$ 2.8 (5) |
| | $\text{Na} + \text{NO}^+ \longrightarrow$ | $\text{Na}^+ + \text{NO}$ | | |
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| K | $\text{Na} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{O}^-$ | $\text{Na}^+ + 2e \longrightarrow$ | $\text{Na} + e$ 3.2 (6) |
| | $\text{Na} + \text{OH} \longrightarrow$ | $\text{Na}^+ + \text{OH}^-$ | $\text{Na}^+ + \text{O}^- \longrightarrow$ | $\text{Na} + \text{O}$ 1.4 (6) |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow$ | $\text{Na}^+ + e + \text{O}_2$ | $\text{Na}^+ + e \longrightarrow$ | $\text{Na} + h\nu$ 7.4 (5) |
| | $\text{Na} + \text{N} + \text{O} \longrightarrow$ | $\text{Na}^+ + e + \text{NO}$ | $\text{Na}^+ + \text{OH}^- \longrightarrow$ | $\text{Na} + \text{OH}$ 1.4 (5) |
| | $\text{Na} + \text{O}_2 \longrightarrow$ | $\text{Na}^+ + \text{O}_2^-$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow$ | $\text{Na} + \text{O}_2$ 2.8 (3) |
| | $\text{Na} + \text{N} + \text{N} \longrightarrow$ | $\text{Na}^+ + e + \text{N}_2$ | $\text{Na}^+ + \text{NO} \longrightarrow$ | $\text{Na} + \text{NO}^+$ 1.7 (3) |
| | $\text{Na} + \text{NO}^+ \longrightarrow$ | $\text{Na}^+ + \text{NO}$ | | |
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| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> | |
|-------------------|---|---|--|
| L | | | |
| | $\text{Na} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{O}^- \longrightarrow$ | $\text{Na} + \text{O} \longrightarrow 1.4 \text{ (13)}$ |
| | $\text{Na} + \text{NO}^+ \longrightarrow$ | $\text{Na}^+ + \text{e} \longrightarrow$ | $\text{Na} + \text{h} \checkmark 3.4 \text{ (12)}$ |
| | $\text{Na} + \text{OH} \longrightarrow$ | $\text{Na}^+ + 2\text{e} \longrightarrow$ | $\text{Na} + \text{e} \longrightarrow 2.2 \text{ (12)}$ |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{OH}^- \longrightarrow$ | $\text{Na} + \text{OH} \longrightarrow 1.4 \text{ (11)}$ |
| | $\text{Na} + \text{N} + \text{N} \longrightarrow$ | $\text{Na}^+ + \text{O}^- + \text{M} \longrightarrow$ | $\text{NaO} + \text{M} \longrightarrow 5.5 \text{ (9)}$ |
| | $\text{Na} + \text{N} + \text{O} \longrightarrow$ | $\text{Na}^+ + \text{O}_2^- \longrightarrow$ | $\text{Na} + \text{O}_2 \longrightarrow 2.8 \text{ (9)}$ |
| | $\text{Na} + \text{O}_2 \longrightarrow$ | $\text{Na}^+ + \text{Na} + \text{M} \longrightarrow$ | $\text{Na}_2^+ + \text{M} \longrightarrow 1.1 \text{ (9)}$ |
| | $(\text{Na} \cdot \text{H}_2\text{O})^+ + \text{M} \longrightarrow$ | | |
| | $\text{Na} + \text{e} \longrightarrow$ | | |

TABLE IV

Free Electron Kinetics

| <u>Conditions</u> | <u>Reactions forming</u> | | <u>Reactions consuming</u> | |
|-------------------|-----------------------------|---------------|---------------------------------------|----------|
| A | $O^- + M \longrightarrow$ | $O + e + M$ | $\longrightarrow O^- + M$ | 2.6 (10) |
| | $Na + e \longrightarrow$ | $Na^+ + 2e$ | $\longrightarrow O^- + h\nu$ | 6.9 (9) |
| | $Na^+ + M \longrightarrow$ | $Na + e + M$ | $\longrightarrow Na + h\nu$ | 2.8 (7) |
| | | | $OH + e + M \longrightarrow OH^- + M$ | 3.4 (6) |
| B, C | $O^- + M \longrightarrow$ | $O + e + M$ | $\longrightarrow O^- + M$ | 6.1 (12) |
| | $Na + e \longrightarrow$ | $Na^+ + 2e$ | $\longrightarrow O^- + h\nu$ | 2.4 (11) |
| | | | $Na^+ + e \longrightarrow Na + h\nu$ | 1.3 (9) |
| | | | $OH + e + M \longrightarrow OH^- + M$ | 1.0 (8) |
| D | $O^- + M \longrightarrow$ | $O + e + M$ | $\longrightarrow O^- + M$ | 1.4 (13) |
| | $O_2^- + M \longrightarrow$ | $O_2 + e + M$ | $\longrightarrow O^- + h\nu$ | 3.7 (11) |
| | | | $Na + e + M \longrightarrow Na^- + M$ | 1.0 (8) |

| <u>Conditions</u> | <u>Reactions forming</u> | | <u>Reactions consuming</u> | |
|-------------------|---|----------|--|----------|
| D (cont.) | $\text{OH}^- + \text{M} \longrightarrow$ | 1.8 (10) | $\text{OH} + \text{e} + \text{M} \longrightarrow \text{OH}^- + \text{M}$ | 1.5 (9) |
| | $\text{Na}^- + \text{M} \longrightarrow$ | 1.6 (8) | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + h\nu$ | 1.2 (9) |
| | $\text{Na} + \text{N} + \text{N} \longrightarrow \text{Na}^+ + \text{e} + \text{N}_2$ | 1.4 (8) | | |
| E | $\text{O}^- + \text{M} \longrightarrow$ | 3.8 (12) | $\text{O} + \text{e} + \text{M} \longrightarrow \text{O}^- + \text{M}$ | 2.8 (12) |
| | $\text{OH}^- + \text{M} \longrightarrow$ | 1.9 (9) | $\text{O} + \text{e} \longrightarrow \text{O}^- + h\nu$ | 6.5 (10) |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow \text{Na}^+ + \text{e} + \text{O}_2$ | 1.4 (8) | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + h\nu$ | 2.3 (8) |
| | $\text{O}_2^- + \text{M} \longrightarrow$ | 9.2 (7) | $\text{O}_2 + \text{e} + \text{M} \longrightarrow \text{O}_2^- + \text{M}$ | 7.8 (7) |
| | | | $\text{OH} + \text{e} + \text{M} \longrightarrow \text{OH}^- + \text{M}$ | 7.6 (7) |
| | | | | |
| F | $\text{O}^- + \text{M} \longrightarrow$ | 1.7 (12) | $\text{O} + \text{e} + \text{M} \longrightarrow \text{O}^- + \text{M}$ | 1.6 (12) |
| | $\text{O}_2^- + \text{M} \longrightarrow$ | 8.6 (9) | $\text{O} + \text{e} \longrightarrow \text{O}^- + h\nu$ | 2.6 (10) |
| | $\text{Na} + \text{O} + \text{O} \longrightarrow \text{Na}^+ + \text{e} + \text{O}_2$ | 2.8 (8) | $\text{O}_2 + \text{e} + \text{M} \longrightarrow \text{O}_2^- + \text{M}$ | 8.6 (9) |
| | $\text{Na}^- + \text{M} \longrightarrow$ | 2.0 (7) | $\text{Na}^+ + \text{e} \longrightarrow \text{Na} + h\nu$ | 1.3 (8) |
| | | | $\text{Na} + \text{e} + \text{M} \longrightarrow \text{Na}^- + \text{M}$ | 2.0 (7) |

| Conditions | Reactions forming | | Reactions consuming | |
|------------|---|----------|---|----------|
| G | $O_2^- + M \longrightarrow O_2 + e + M$ | 1.5 (11) | $O_2 + e + M \longrightarrow O_2^- + M$ | 1.5 (11) |
| | $O^- + M \longrightarrow O + e + M$ | 7.6 (8) | $O + e + M \longrightarrow O^- + M$ | 7.5 (10) |
| | $Na^- + M \longrightarrow Na + e + M$ | 3.6 (7) | $O + e \longrightarrow O^- + h\nu$ | 7.6 (8) |
| | | | $Na^+ + e \longrightarrow Na + h\nu$ | 5.4 (7) |
| H | $O_2^- + M \longrightarrow O_2 + e + M$ | 7.2 (11) | $O_2 + e + M \longrightarrow O_2^- + M$ | 7.2 (11) |
| | $Na^- + M \longrightarrow Na + e + M$ | 1.7 (8) | $Na + e + M \longrightarrow Na^- + M$ | 1.7 (8) |
| | | | $Na^+ + e \longrightarrow Na + h\nu$ | 1.5 (8) |
| | | | $O_2 + e \longrightarrow O_2^- + h\nu$ | 2.1 (7) |
| I | $Na + H_2O \longrightarrow (Na \cdot H_2O)^+ + e$ | 1.0 (11) | $(Na \cdot H_2O)^+ + e \longrightarrow Na + H_2O$ | 1.0 (11) |
| | $O_2^- + M \longrightarrow O_2 + e + M$ | 3.2 (9) | $O_2 + e + M \longrightarrow O_2^- + M$ | 3.4 (8) |
| | $Na^- + M \longrightarrow Na + e + M$ | 3.2 (7) | | |

| <u>Conditions</u> | <u>Reactions forming</u> | | <u>Reactions consuming</u> | |
|-------------------|------------------------------|-------------------------|-------------------------------|----------|
| J | $O^- + M \longrightarrow$ | $O + e + M$ | $O^- + M \longrightarrow$ | 3.4 (13) |
| | $O_2^- + M \longrightarrow$ | $O_2 + e + M$ | $O^- + h\nu \longrightarrow$ | 1.8 (11) |
| | $Na + O + O \longrightarrow$ | $Na^+ + e + O_2$ | $O_2 + e + M \longrightarrow$ | 1.4 (9) |
| | $Na + N + O \longrightarrow$ | $Na^+ + e + NO$ | $Na + e + M \longrightarrow$ | 6.8 (8) |
| | $Na + N + N \longrightarrow$ | $Na^+ + e + N_2$ | $OH + e + M \longrightarrow$ | 6.8 (8) |
| | $Na^- + M \longrightarrow$ | $Na + e + M$ | $Na^+ + e \longrightarrow$ | 1.1 (8) |
| | $Na + H_2O \longrightarrow$ | $(Na \cdot H_2O)^+ + e$ | | |
| | $Na + M \longrightarrow$ | $Na^+ + e + M$ | | |
| | $O^- + M \longrightarrow$ | $O + e + M$ | $O^- + M \longrightarrow$ | 3.4 (13) |
| | $O_2^- + M \longrightarrow$ | $O_2 + e + M$ | $O^- + h\nu \longrightarrow$ | 1.8 (11) |
| K | $Na + H_2O \longrightarrow$ | $(Na \cdot H_2O)^+ + e$ | $O_2 + e + M \longrightarrow$ | 1.4 (9) |
| | $Na + O + O \longrightarrow$ | $Na^+ + e + O_2$ | $OH + e + M \longrightarrow$ | 6.8 (8) |

| <u>Conditions</u> | <u>Reactions forming</u> | | <u>Reactions consuming</u> | |
|-------------------|---|----------|---|----------|
| L | $O^- + M \longrightarrow O + e + M$ | 9.4 (17) | $O + e + M \longrightarrow O^- + M$ | 5.1 (17) |
| | $O_2^- + M \longrightarrow O_2 + e + M$ | 9.9 (13) | $O + e \longrightarrow O^- + h\nu$ | 3.9 (14) |
| | $Na + O + O \longrightarrow Na^+ + e + O_2$ | 1.2 (12) | $O_2 + e + M \longrightarrow O_2^- + M$ | 4.2 (13) |
| | | | $OH + e + M \longrightarrow OH^- + M$ | 1.4 (13) |
| | | | $Na^+ + e \longrightarrow Na + h\nu$ | 3.3 (12) |

TABLE V

Na (3^2P) Kinetics

| Conditions | Reactions forming | | Reactions consuming | |
|------------|---|---------------------------------|---------------------|--|
| A | $\text{Na } (3^2S) + e \longrightarrow$ | $\text{Na } (3^2P) + e$ | 1.5 (13) | $\text{Na } (3^2P) \longrightarrow \text{Na } (3^2S) + h\nu$ 1.3 (15) |
| | $\text{Na } (4^2S) \longrightarrow$ | $\text{Na } (3^2P) + h\nu$ | 1.4 (13) | $\text{Na } (3^2P) + e \longrightarrow \text{Na } (3^2S) + e$ 1.5 (13) |
| | $\text{Na } (3^2S) + M \longrightarrow$ | $\text{Na } (3^2P) + M$ | 1.3 (12) | $\text{Na } (3^2P) + M \longrightarrow \text{Na } (3^2S) + M$ 1.4 (12) |
| | $\text{Na } (4^2S) + e \longrightarrow$ | $\text{Na } (3^2P) + e$ | 8.4 (9) | $\text{Na } (3^2P) + O \longrightarrow \text{Na}^+ + O^-$ 1.3 (11) |
| | $\text{Na } (4^2S) + M \longrightarrow$ | $\text{Na } (3^2P) + M$ | 7.4 (8) | |
| | | | | |
| B | $\text{Na } (3^2S) + e \longrightarrow$ | $\text{Na } (3^2P) + e$ | 7.0 (14) | $\text{Na } (3^2P) \longrightarrow \text{Na } (3^2S) + h\nu$ 1.3 (16) |
| | $\text{Na } (4^2S) \longrightarrow$ | $\text{Na } (3^2P) + h\nu$ | 1.4 (14) | $\text{Na } (3^2P) + e \longrightarrow \text{Na } (3^2S) + e$ 7.1 (14) |
| | $\text{Na } (3^2S) + M \longrightarrow$ | $\text{Na } (3^2P) + M$ | 8.6 (13) | $\text{Na } (3^2P) + M \longrightarrow \text{Na } (3^2S) + M$ 8.8 (13) |
| | $\text{NaO} + N \longrightarrow$ | $\text{Na } (3^2P) + \text{NO}$ | 5.4 (12) | $\text{Na } (3^2P) + O \longrightarrow \text{Na}^+ + O^-$ 1.0 (12) |
| | $\text{NaH} + O \longrightarrow$ | $\text{Na } (3^2P) + \text{OH}$ | 4.5 (12) | $\text{Na } (3^2P) + e \longrightarrow \text{Na } (4^2S) + e$ 2.8 (11) |
| | $\text{Na } (4^2S) + e \longrightarrow$ | $\text{Na } (3^2P) + e$ | 3.9 (11) | |
| | $\text{NaH} + H \longrightarrow$ | $\text{Na } (3^2P) + H_2$ | 7.6 (10) | |
| | $\text{NaO} + H \longrightarrow$ | $\text{Na } (3^2P) + \text{OH}$ | 3.0 (9) | |

| Conditions | Reactions forming | Reactions consuming |
|--------------|---|---------------------|
| B (cont.) | $\text{NaO} + \text{O} \longrightarrow \text{Na} (3^2\text{P}) + \text{O}$ | 4.9 (10) |
| | $\text{Na} (4^2\text{S}) + \text{M} \longrightarrow \text{Na} (3^2\text{P}) + \text{M}$ | 4.8 (10) |
| C | $\text{Na} (3^2\text{S}) + \text{e} \longrightarrow \text{Na} (3^2\text{P}) + \text{e}$ | 7.0 (14) |
| | $\text{Na} (4^2\text{S}) \longrightarrow \text{Na} (3^2\text{P}) + h\nu$ | 1.4 (14) |
| | $\text{Na} (3^2\text{S}) + \text{M} \longrightarrow \text{Na} (3^2\text{P}) + \text{M}$ | 8.6 (13) |
| | $\text{Na} (4^2\text{S}) + \text{e} \longrightarrow \text{Na} (3^2\text{P}) + \text{e}$ | 3.9 (11) |
| | $\text{Na} (4^2\text{S}) + \text{M} \longrightarrow \text{Na} (3^2\text{P}) + \text{M}$ | 4.8 (10) |
| D | $\text{Na} (3^2\text{S}) + \text{e} \longrightarrow \text{Na} (3^2\text{P}) + \text{e}$ | 7.1 (14) |
| | $\text{Na} (4^2\text{S}) \longrightarrow \text{Na} (3^2\text{P}) + h\nu$ | 1.4 (14) |
| | $\text{Na} (3^2\text{S}) + \text{M} \longrightarrow \text{Na} (3^2\text{P}) + \text{M}$ | 1.3 (14) |
| | $\text{Na} (4^2\text{S}) + \text{e} \longrightarrow \text{Na} (3^2\text{P}) + \text{e}$ | 3.9 (11) |
| | $\text{Na} (4^2\text{S}) + \text{M} \longrightarrow \text{Na} (3^2\text{P}) + \text{M}$ | 7.1 (10) |
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| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> |
|-------------------|---|---|
| E | $\text{Na } (3^2\text{S}) + e \longrightarrow \text{Na } (3^2\text{P}) + e$ | $\text{Na } (3^2\text{P}) \longrightarrow \text{Na } (3^2\text{S}) + h\nu$ 1.6 (15) |
| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + h\nu$ | $\text{Na } (3^2\text{P}) + e \longrightarrow \text{Na } (3^2\text{S}) + e$ 2.4 (14) |
| | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (3^2\text{S}) + \text{M}$ 4.3 (13) |
| | $\text{Na } (4^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) + e \longrightarrow \text{Na } (4^2\text{S}) + e$ 2.8 (11) |
| | $\text{Na } (4^2\text{S}) + e \longrightarrow \text{Na } (3^2\text{P}) + e$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (4^2\text{S}) + \text{M}$ 3.8 (10) |
| | $\text{Na}^+ + \text{OH}^- \longrightarrow \text{Na } (3^2\text{P}) + \text{OH}$ | $\text{Na } (3^2\text{P}) + \text{O} \longrightarrow \text{Na}^+ + \text{O}^-$ 9.8 (10) |
| | $\text{NaO} + \text{O} \longrightarrow \text{Na } (3^2\text{P}) + \text{O}_2$ | |
| F | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) \longrightarrow \text{Na } (3^2\text{S}) + h\nu$ 7.7 (14) |
| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + h\nu$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (3^2\text{S}) + \text{M}$ 1.0 (13) |
| | $\text{Na } (3^2\text{S}) + e \longrightarrow \text{Na } (3^2\text{P}) + e$ | $\text{Na } (3^2\text{P}) + \text{O} \longrightarrow \text{Na}^+ + \text{O}^-$ 1.2 (11) |
| | $\text{NaO} + \text{O} \longrightarrow \text{Na } (3^2\text{P}) + \text{O}_2$ | $\text{Na } (3^2\text{P}) + e \longrightarrow \text{Na } (3^2\text{S}) + e$ 1.2 (11) |
| | $\text{Na } (4^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) + \text{O}_2 \longrightarrow \text{NaO} + \text{O}$ 3.2 (9) |
| | | |
| G | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) \longrightarrow \text{Na } (3^2\text{S}) + h\nu$ 6.1 (14) |
| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + h\nu$ | $\text{Na } (3^2\text{P}) + \text{O}_2 + \text{M} \longrightarrow \text{NaO}_2 + \text{M}$ 1.9 (11) |
| | $\text{NaO} + \text{O} \longrightarrow \text{Na } (3^2\text{P}) + \text{O}_2$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (3^2\text{S}) + \text{M}$ 1.0 (11) |

| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> |
|-------------------|---|----------------------------|
| G (cont.) | | |
| | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na } (3^2\text{P}) + \text{O}_2$ | 3.3 (7) |
| | $\text{Na}^+ + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{h}\nu$ | 2.3 (7) |
| H | | |
| | $\text{Na}^+ + \text{O}_2^- \longrightarrow \text{Na } (3^2\text{P}) + \text{O}_2$ | 5.7 (9) |
| | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | 4.9 (6) |
| | $\text{NaH} + \text{H} \longrightarrow \text{Na } (3^2\text{P}) + \text{H}_2$ | 8.4 (4) |
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| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + \text{h}\nu$ | 1.4 (14) |
| | $\text{Na } (4^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | 2.4 (11) |
| | $(\text{Na} \cdot \text{H}_2\text{O})^+ + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{H}_2\text{O}$ | 1.0 (11) |
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| J | | |
| | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | 6.6 (15) |
| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + \text{h}\nu$ | 1.4 (15) |
| | $\text{Na } (3^2\text{S}) + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{e}$ | 6.1 (14) |
| | $\text{Na } (4^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | 3.6 (12) |
| | $\text{Na } (4^2\text{S}) + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{e}$ | 3.4 (12) |
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| | $\text{Na } (3^2\text{P}) \longrightarrow \text{Na } (3^2\text{S}) + \text{h}\nu$ | 1.3 (17) |
| | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (3^2\text{S}) + \text{M}$ | 6.6 (15) |
| | $\text{Na } (3^2\text{P}) + \text{C} \longrightarrow \text{Na}^+ + \text{O}^-$ | 8.7 (14) |
| | $\text{Na } (3^2\text{P}) + \text{e} \longrightarrow \text{Na } (3^2\text{S}) + \text{e}$ | 6.2 (14) |

| <u>Conditions</u> | <u>Reactions forming</u> | <u>Reactions consuming</u> |
|-------------------|---|--|
| K | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) \longrightarrow \text{Na } (3^2\text{S}) + h\nu$ 1.3 (15) |
| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + h\nu$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (3^2\text{S}) + \text{M}$ 6.6 (13) |
| | $\text{Na } (3^2\text{S}) + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{e}$ | $\text{Na } (3^2\text{P}) + \text{O} \longrightarrow \text{Na}^+ + \text{O}^-$ 8.7 (12) |
| | $\text{Na } (4^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) + \text{e} \longrightarrow \text{Na } (3^2\text{S}) + \text{e}$ 6.2 (12) |
| | $\text{Na } (4^2\text{S}) + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{e}$ | |
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| L | $\text{Na } (3^2\text{S}) + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{e}$ | $\text{Na } (3^2\text{P}) + \text{e} \longrightarrow \text{Na } (3^2\text{S}) + \text{e}$ 1.9 (17) |
| | $\text{Na } (3^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) \longrightarrow \text{Na } (3^2\text{S}) + h\nu$ 1.3 (17) |
| | $\text{Na } (4^2\text{S}) \longrightarrow \text{Na } (3^2\text{P}) + h\nu$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (3^2\text{S}) + \text{M}$ 4.6 (16) |
| | $\text{Na } (4^2\text{S}) + \text{e} \longrightarrow \text{Na } (3^2\text{P}) + \text{e}$ | $\text{Na } (3^2\text{P}) + \text{O} \longrightarrow \text{Na}^+ + \text{O}^-$ 6.2 (15) |
| | $\text{Na } (4^2\text{S}) + \text{M} \longrightarrow \text{Na } (3^2\text{P}) + \text{M}$ | $\text{Na } (3^2\text{P}) + \text{M} \longrightarrow \text{Na } (4^2\text{S}) + \text{M}$ 1.8 (13) |
| | $\text{Na}^+ + \text{O}^- \longrightarrow \text{Na } (3^2\text{P}) + \text{O}$ | |
| | $\text{NaO} + \text{O} \longrightarrow \text{Na } (3^2\text{P}) + \text{O}$ | |
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REFERENCES

1. M. H. Bortner, "Chemical Kinetics in a Reentry Flow Field", General Electric Company, M.S.D., Report #R63SD63 (1963).
2. M. H. Bortner, "The Chemical Kinetics of Atmospheric Deionization", General Electric Company, M.S.D., Report #R63SD34 (1963).
3. A. Fundamirsky, Thesis, Univ. of London (1949).
4. G. Haft, Z. Phys. 82, 73 (1933).
5. W. Christoph, Ann. Phys., Leipzig 23, 51 (1935).
6. D. R. Bates, A. Fundamirsky, H. S. W. Massey and J. W. Leech, Phil. Trans. Roy. Soc. A243, 93 (1950).
7. L. von Harnes, Z. f. Phys. 74, 379 (1932).
8. R. Mannkopff, Z. f. Phys. 36, 315 (1926).
9. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge, 1961, p. 209.
10. J. T. Tate and P. T. Smith, Phys. Rev. 46, 773 (1934).
11. Y. Kaneko, J. Phys. Soc. Japan 16, 2288 (1961).
12. G. O. Brink, Phys. Rev. 127, 1204 (1962).
13. G. O. Brink, Univ. California Lawrence Radiation Laboratory Report UCRL 7492, 1963.
14. J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).
15. F. W. Lampe, J. L. Franklin, and F. H. Field, J. Amer. Chem. Soc. 79, 6129 (1957).
16. G. H. Miller and N. G. Utterback, Phys. Rev. 124, 1477 (1961).
17. W. Fite and R. T. Brackman, Phys. Rev. 113, 815 (1959).
18. J. D. Graggs, R. Thonburn, and B. A. Tozer, Proc. Roy. Soc. A240, 473 (1957).

19. N. G. Utterback, Phys. Rev. 129, 219 (1963).
20. D. R. Bates and A. Dalgarno, Atomic and Molecular Processes (ed. D. R. Bates), Academic Press, 1962, pp. 245-271.
21. H. Y. Yeung, Proc. Phys. Soc. 71, 341 (1958).
22. H. Y. Yeung, J. Electronics and Control, 5, 307 (1958).
23. J. Sayers, Atomic and Molecular Processes (ed. D. R. Bates), Academic Press, 1962, pp. 272-279.
24. V. A. J. van Lint, "Measurement of Ionic Recombination in O₂", 16th Gaseous Electronics Conference, Pittsburgh, 1963.
25. C. W. Baulknight and M. H. Bortner, "Theoretical Calculation of Cross-Sections of Importance to Atmospheric Deionization", General Electric Company, Space Sciences Laboratory, Report R64SD12, 1964.
26. D. R. Bates, Proc. Roy. Soc. A257, 22 (1960).
27. H. Wise, Bull. Amer. Phys. Soc. 6, 517 (1961).
28. C. E. H. Bawn and A. G. Evans, Trans. Far. Soc. 33, 1571 (1937).
29. W. E. Kaakan, "The Chemistry of Alkali Metals in Flames", General Electric Research Lab. Report 61RL2823C (1961).
30. L. M. Branscomb, Atomic and Molecular Processes (ed. D. R. Bates), Academic Press, 1962, pp. 100-140.
31. C. W. Allen, Astrophysical Quantities, Univ. of London Press, 1955, p. 71.
32. D. R. Bates and M. Seaton, Proc. Phys. Soc. B63, 129 (1950).
33. T. M. Sugden, "A Survey of Flame Ionization Work at the University of Cambridge", Amer. Rocket Soc. Conf. on Ions in Flames and Rockets, Palm Springs, 1962.
34. D. R. Bates and M. Nicolet, J. geophys. Res. 55, 235 (1950).
35. M. Ogawa, Science of Light 3, 47 (1954).
36. E. R. Manring, J. geophys. Res. 63, 19 (1958).
37. P. J. Padley and T. M. Sugden, Proc. Roy. Soc. A248, 248 (1958).

TECHNICAL INFORMATION SERIES

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| AUTHOR M. H. Bortner | SUBJECT CLASSIFICATION Chemical Kinetics | NO. R64SD33 DATE 4/24/64 |
| TITLE THE CHEMICAL KINETICS OF SODIUM IN REENTRY | | G. E. CLASS I GOV. CLASS Unclassified |
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| <p>ABSTRACT</p> <p>Sodium is important to reentry because of its contributions to radiation and electron density. It is shown here that neither its radiation nor its electron density can be expected to be in equilibrium. A study of the complete chemical kinetics of sodium is described herein. The radiation is subject to considerable "collision limiting" (non-equilibrium excitation and deexcitation). The ionization processes cannot be assumed to be instantaneous and the deionization processes are very slow. The major reaction is the ionization-deionization system, found to be $\text{Na} + \text{O} \rightleftharpoons \text{Na}^+ + \text{O}^-$, although other reactions, both of this type and other types, contribute appreciably, depending on the conditions. Included in this report is a recommended chemical system, with rate constants, for use in any non-equilibrium calculations of the effects of sodium in reentry.</p> | | |
| <p>KEY WORDS Sodium, Non-equilibrium, Contaminant, Chemical Kinetics, Reentry, Ionization, Deionization, Excitation</p> | | |

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AUTHOR

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